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ANALYSING DIFFERENT SOIL ORGANIC MATTER POOLS IN CLAY SIZED MICROAGGREGATES ALONG A SOIL AGE GRADIENT IN THE MARCHFELD, AUSTRIA

Master Thesis submitted to the
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ABSTRACT

Microaggregate formation is mainly influenced by soil organic matter (SOM) and in turn organic matter is protected in microaggregates. Clay sized microaggregates contain a large pool of soil organic matter with long turnover times but processes behind this and the co-evolution of the formation of microaggregates and SOM is not completely clear. Therefore clay sized microaggregates in the A and AC horizon of Fluvisols and Chernozems from a soil chronosequence (approximately 10 to 4500 years) in the floodplain of the Danube River, east of Vienna (Austria), was analysed to receive trends of soil organic matter accumulation and soil formation. The influence of land use (grassland, forest, and cropland) on SOM dynamics is also considered. The combined use of ultrasound (55 Watt) and centrifugation, a soft method that does not harm SOM, was chosen to gain clay sized microaggregates. Basic physical and chemical analysis (particle size distribution, pH, carbonate content, organic and total C and N content) were carried out. The microaggregates were further analysed with a Simultaneous Thermal Analysis (STA). The soils have alkaline conditions and show especially in old subsoil samples a high carbonate content. In the A horizon the clay sized microaggregates at sites used as cropland contain much less C_{org} in the A horizon than forest or grassland sites. The SOM content of the cropland in the A horizon is at the beginning of soil formation similar to fresh sediment in the Danube River and shows only a small but steady increase along the age gradient. Forest sites show a steep increase of SOM in the first years of soil development and it seems that after ~350 years clay minerals are saturated and cannot store significantly more SOM with time, maybe due to the low weathering of the soils in the study area.

Splitting up the SOM in different pools by STA shows that cropland sites contain the lowest amount of labile compounds, but the highest amount of more stable pools. This difference is increasing with time. The results received from the STA allowed to calculate a ratio (Exo_{2+3}:Exo_1) to receive the relative contribution of stable to labile compounds to the total SOM. This showed that the cropland sites in the chronosequence in the AC horizons and contain the most stable compounds. I general, approximately after 2000 years of soil development the SOM consists relatively of more stable than labile compounds. The received data allowed a rough calculation of the annual soil formation rate based on the

depth of the AC horizon. It is shown that at the beginning of soil formation the rate is very high (up to 4 mm/year) and slows down very fast to ~0.1mm after 2000 years. The AC horizons show strongly changed properties compared to the topsoils and need to be more analysed in future studies.

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1. INTRODUCTION AND OBJECTIVES

Soil is the largest active terrestrial reservoir in the global carbon cycle (Leifeld and Kögel-Knabner, 2005). The pedosphere stores carbon in form of soil organic matter (SOM) (Urbanek et al., 2011) due to several stabilisation mechanisms in different pools with different SOM turnover times (up to thousands of years) (von Lützow et al., 2008). Slow SOM turnover rates responsible for long- term carbon storage mainly occur in microaggregates (Helfrich et al., 2007). Organic matter in clay sized microaggregates are major sites of OM stabilisation by ad- and absorption (to minerals) and entrapment in small aggregates protecting the organic matter against microbial decomposition and mineralization (Chenu and Plante, 2006). The formation of microaggregates in turn depends on soil organic matter formation (Six et al., 2002). The processes of the co- evolution of soil minerals and organic matter resulting in clay sized microaggregates are not well understood. A multitude of interactions in the environment lead to a complex research topic which is difficult to understand (Six et al., 2004).

Current studies showed that the soil mineral fraction can become saturated and cause a limitation of soil to store organic material (Gulde et al., 2008). Concentrating the study on clay sized microaggregates developed in a soil chronosequence promises to help understanding SOM storage and changes in different organic matter pools as well as in the mineral matrix.

Land use and agricultural management practices influence the amount and quality of plant residues added to the soil and the SOM decomposition rates (Gerzabek et al., 2006) and cause distinct soil organic matter dynamics (Balesdent et al., 1998). Soil aggregates respond to sensitive to management practices what can lead to an increased decomposition of soil organic matter (Six et al., 1998). It is important to consider the influence of the addition of organic matter and the management practices due to different land uses.

Subsoil only received interest during the last few years. Many authors agree that this horizon can give missing information concerning SOM and its stability because deeper horizons contain high proportions of total carbon and OM stored in subsoil is older and contains more stable compounds (Rumpel and Kögel- Knabner, 2011).

The main objective of this work is to determine how soil properties, especially soil organic matter content and its composition, change in clay sized aggregates in the A and AC horizon due to the influence of:

- Soil development in the range of approximately of 10- 4500 years
- Land use; cropland, grassland and forest

The analysis on clay sized microaggregates will show what kind of influence soil age has on the clay sized soil particles and if land use has a stronger influence on SOM storage than decades of soil development. Further, the co- evolution of organic matter and minerals in these microaggregates will be measured and characterised.

According to a study performed on bulk soils in the Marchfeld (Zehetner et al., 2009), a rapid increase of SOM accumulation in the clay sized aggregates in the A horizon is expected. The fast decrease of carbon accumulation in the bulk soil after 300 years of soil development should be related to the completed occupation of the mineral surfaces with organic matter.

A further hypothesis is that SOM is transported along the age gradient to the subsoil and becomes more stabilised by decomposition processes compared to the A horizon.

2. STATE OF ART

2.1. Chronosequences and floodplains

Soil studies along a substrate age gradient are called chronosequences (Hugget, 1998). They add to space the factor time (soil as a 4- dimensional matrix) which helps to analyse temporal dynamics of plant communities and soil development across a time scale (Walker et al., 2010). Important for such kind of studies is the fact that soils have been formed on the same parent material, in the same climate and in the same topography but have a different soil age. Guided data shall be related in a predictable and temporally linear manner and are especially useful when soil processes have occurred in a relatively predictive, linear fashion over time (Walker et al., 2010). Five main factors (climate, disturbance/management, soil age, parent material, topographic), which have an interrelationship influence the soil formation (Jenny, 1945; Sollins et al., 1996).

On riverine floodplains, soil studies across substrate age gradients have covered hundreds to thousands of years and mainly quantified pedogenic long- term changes (clay accumulation and translocation, formation of pedogenic carbonates and silicon, and increases in Fe oxide content and crystallinity (see review in Zehetner et al., 2009). Lair et al. (2009, a, page 3336) mentions that "floodplains are characterized by a shifting mosaic of interconnected aquatic, semi- aquatic and terrestrial habitats and are among the most productive and heterogeneous ecosystems on the continents".

A study by Zehetner et al. (2009) quantified organic carbon content and changes of SOM pools along a chronosequence in the same area as this study takes place. The results showed a rapid carbon accumulation during the first 100 years and a strong decrease of the accumulation afterwards. The composition of different SOM pools also reached a steady state already in the very early years of development.

Literature about chronosequences and soil formation in other comparable floodplains is limited. Some recent studies concentrated on a proglacial area in the Damier glacier. Dümig et al. (2012) did a study on clay fractions to explain the evolution of organo- mineral associations during soil formation. The research showed a shift in quantity and quality of organic matter (like the relative reduction of carboxylic and aromatic carbon but a relative increase of O- alkyl carbon) in the clay fraction with progressing soil development. Egli et al. (2000) showed that the bulk soils in this glacier fore field have a high amount of less decomposable soil organic matter and strong organo-mineral associations already at the start of soil formation maybe from earlier warmer time periods during the Holocene.

2.2. Soil structure and aggregate formation

Soil structure plays an important role in agricultural productivity and in preservation of a high environmental quality (Amezketa et al., 1999). Soil structure is the organisation of aggregates and the pore space among them (Blanco- Canqui and Lal, 2004). The formation of these aggregates is "the process by which aggregates of different sizes are joined and held together by different organic and inorganic materials. Thus, it includes the processes of formation and stabilization" (Amèzketa et al., 1999, page 86). In general, aggregate formation and stability forces the physical protection of organic matter from mineralization (von Lützow et al., 2006) and is presenting a fundamental property which determines the productivity of soil and its resistance to erosion and degradation (An et al., 2010). The aggregate stability is mainly caused by organic matter working as a major stabilisation agent on the one hand but on the other hand organic matter is protected itself by mineral associations from degradation (Virto et al., 2010).

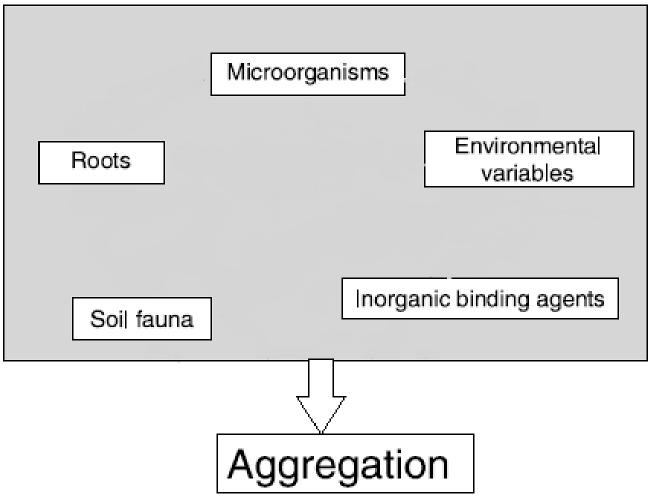
Soil structure not only physically protect soil organic matter, but also influences factors which control SOM dynamics and nutrient cycling like microbial community structure, oxygen diffusion, water flow regulation, nutrient adsorption and desorption, run-off and erosion (Six et al., 2004).

Aggregates are divided into macro- (> 250 µm) and microaggregates (< 250 µm). Especially the small microaggregates are important for SOM because they (mainly) physically protect SOM and turn it over more slowly (Moni et al., 2010). Compared to microaggregates, macroaggregates contain a younger and more labile pool of organic matter (John et al., 2005).

2.2.1. Soil aggregate formation

The concepts behind aggregate formation are well studied but not completely understood. There are several models of soil aggregate formation.

A link between soil organic matter and aggregate dynamics was already recognised more than hundred years ago (Six et al., 2004). At that time it was already clear that five major factors influence aggregate formation and stabilisation (see Figure 1). In the 1960s, the formation of microaggregates was contributed to a reaction between clay minerals, polyvalent cations and SOM (Six et al., 2004). Based on this concept, in the 1980s a pioneering concept of aggregate formation was developed, suggesting that aggregates are ranged hierarchically (binding of microaggregates is responsible for formation of macroaggregates) with SOM as the main binding agent (Tisdall and Oades, 1982; Blanco- Canqui and Lal, 2004).



Source: modified after Six et al., 2004

Nowadays several aggregation models exist. Figure 2 illustrates the most commonly accepted models of aggregate formation in the last thirty years. The concept of Tisdall and Oades (1982) was further developed by the assumption that microaggregates are formed in macroaggregates (Oades 1984, Six et al., 2004). There are models which assume that carbon stocks are linearly proportional to C input and can therefore increase without limit. A previous study in the Marchfeld however let us assume that carbon stocks reach a “steady state” in the time scale of 100 years (Zehetner et al., 2009).

Therefore a model by Six et al. (1998; 2000) is presented. This model is based on a soil carbon saturation concept (Six et al., 2002).

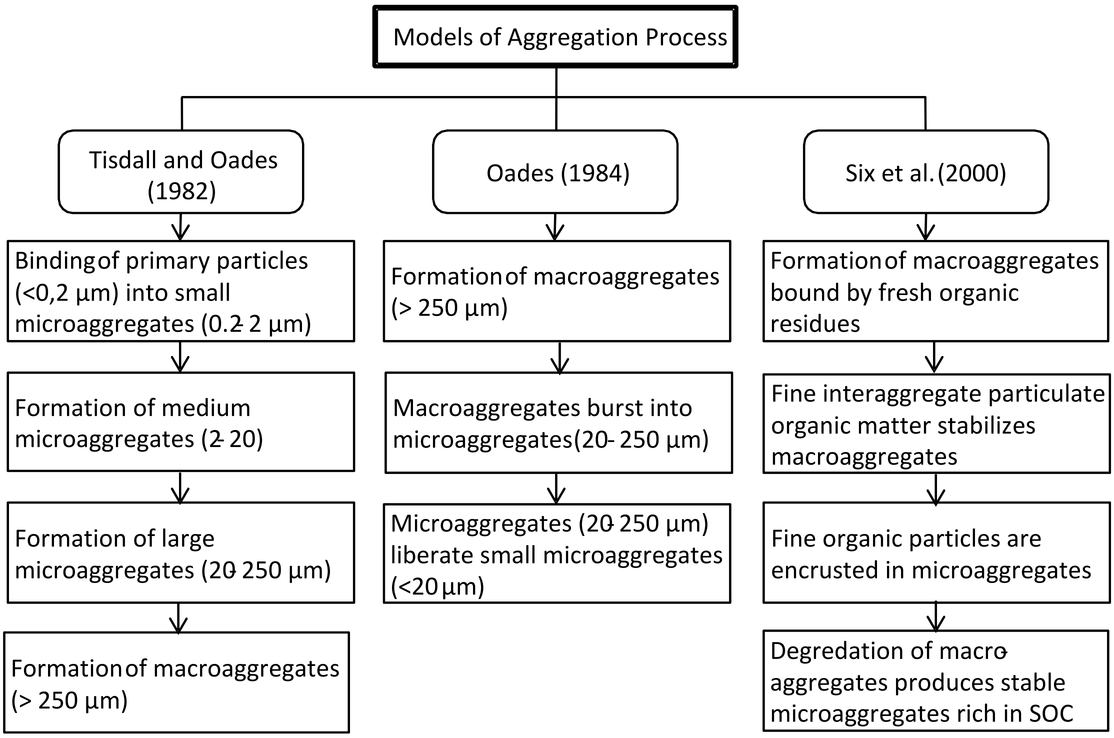


Figure 2: Soil aggregate formation models
Source: Blanco- Canqui and Lal, 2004

The model by Six et al. (2000) describes the "*life cycle of a macroaggregate and formation of microaggregates*":

Figure 3 proposes similar rates of macroaggregate formation at the beginning (time step 1), independent of management systems. When fresh residues enter the soil, soil microorganisms utilise the more easily available carbon and macroaggregates are formed around it due to fungal hyphae, bacterial etc. and the fresh material becomes coarse intraaggregate particulate organic matter (iPOM). This coarse iPOM decomposes further and is subsequently fragmentised to fine iPOM within the macroaggregates because decomposition causes a decrease in POM size. Within these macro-aggregates, micro-aggregates are formed due to the encrustment of fine iPOM with clay particles and microbial products (time step 2- time step 3). When binding agents in macroaggregates are degraded, they lose their stability and cause a release of very stable microaggregates and clay- and silt- sized organo- mineral complexes (Six et al., 2004). These microaggregates can however be again incorporated into newly formed macroaggregates, closing the cycle. The process of microaggregate formation is therefore the result of the interrelationship between the turnover of macroaggregates, the turnover of SOM and controlling factors like disturbance (i.e. tillage) (Six et al., 2000).

SOM protected in aggregates is sensitive to land management practices like tillage, crop rotation or manure application (Gulde et al., 2008). Tillage causes a physical breakdown and faster macroaggregate turnover and consequently microaggregates of lower SOM content are released (Six et al., 2000).

Virto et al. (2010) mentioned that according to this model, silt and clay-sized aggregates are the most stable forms and contain the most processed and oldest organic particles. The mineral particles within microaggregates are associated with well decomposed (humified) organic matter (Virto et al., 2010). This model and the role of clay- sized aggregates in soil formation are a fundamental knowledge for this study.

2.2.2. Aggregate stability

Aggregate stability is defined by the degree of adherence of primary soil particles and SOM which strongly depend on inorganic and organic stabilising agents (see Table 1) (Blanco-Canqui and Lal, 2004). These agents are at the same time responsible for the stability of

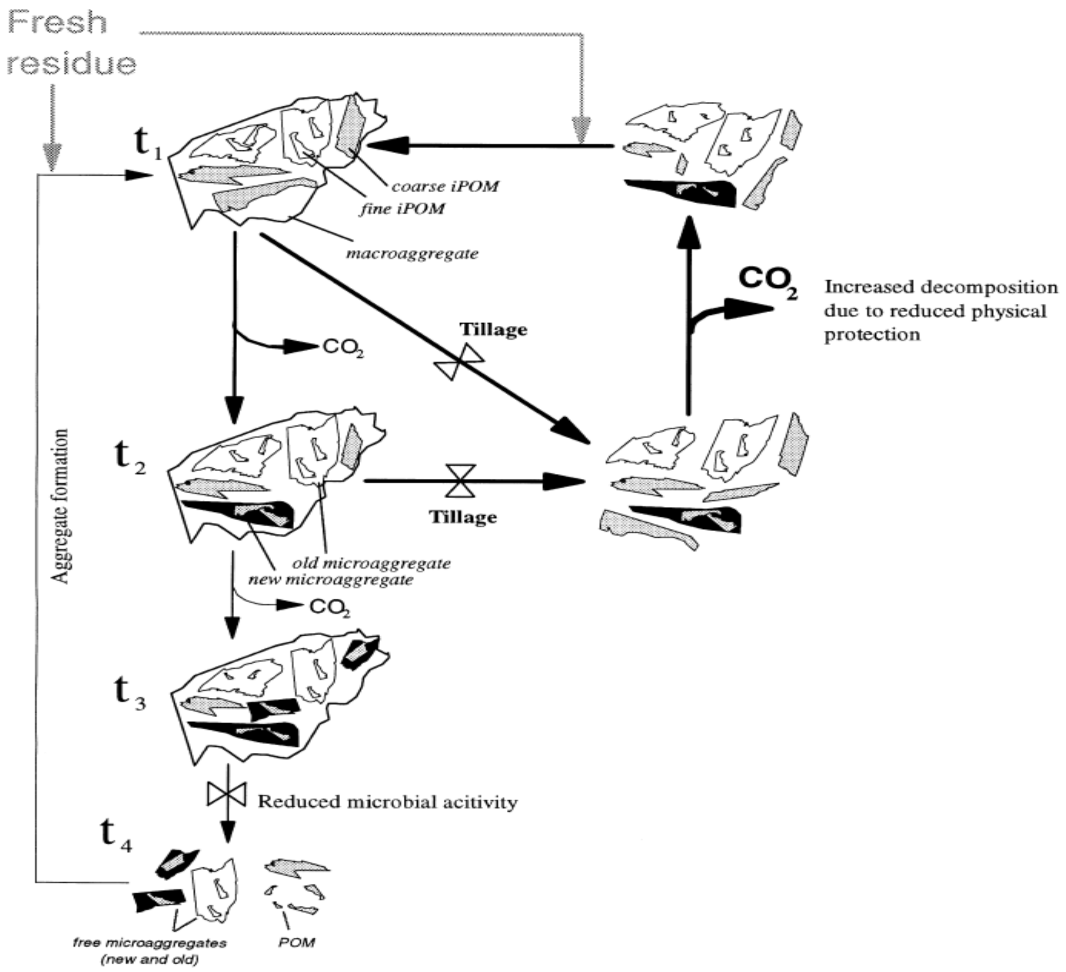


Figure 3: Model of the “life cycle of macroaggregates and the formation of microaggregates”

Source: Six et al., 2000

SOM (compare chapter 2.3.1.). Inorganic agents are (Amèzketa et al., 1999):

- type of clay minerals
- oxides and hydroxides of Fe and Al
- carbonates and gypsum
- Polyvalent metal cations (Ca^{2+}, Fe^{2+}, Al^{3+}, Mn^{2+})

One of the most important inorganic binding agents in microaggregates are oxides (Six et al., 2004). Oxides act as binding agents by adsorbing organic material on its surface, by an electrostatic binding between positively charged oxides and negatively charged clay minerals and by the formation of bridges between particles due to oxide coatings on their surface (Six et al., 2004).

The organic binding agents can be differentiated as temporary, transient and persistent agents (see Table 1). The relative importance of binding agents on aggregate stability is however not completely clear (Abiven et al., 2007). In general, the incorporation of more decomposable organic material in soils has a greater and more rapid effect on aggregate stability compared to less decomposable material, which has a small but long lasting effect (Abiven et al., 2007).

Table 1: Properties of organic binding agents for aggregate built up and stability

Source: Modified after Blanco- Canqui and Lal, 2004

temporary	Consists of: plant roots, fungal hyphae, mycorrhizal hyphae, bacteria cells ,algae associated with macroaggregates; greatly affected by tillage
transient	Consists of: polysaccharides, non- humic compounds with high molecular weight Derives from: plant and animal tissue, exudations of plant roots, fungal hyphae, bacteria rapidly decomposed by microbial processes; stabilisation effect: few weeks

persistent	Consists of: humic compounds with low molecular weight, polymers, polyvalent cation associated with microaggregates; form organo- mineral complexes

Macroaggregates show spatial heterogeneities of pores and other important factors (Urbanek et al., 2011). This different distribution of pores makes the centres of aggregates less accessible to microorganisms and leads to a concentration of the microbial activity on the soil aggregate surface (Chenu et al., 2001).

Steffens et al. (2009) elaborated reviews about the relationship between soil organic matter and aggregation and summarised that:

- the fresher/ more active SOM material with high mono- or polysaccharide content is mainly responsible for aggregate stabilisation
- there is no further increase in stabilisation above a certain SOM content
- adequate supply of SOM is more important than the amount for aggregate formation
- organo- mineral complexes play a major role on microaggregates, macroaggregates are strongly influenced by root systems and cultivation

2.3. Soil organic matter

Soil organic matter can be defined as “all dead living material in or lying on the soil that contains carbon. Detritus refers to SOM still recognizable as dead plant or animal material, including leaf litter, coarse woody debris, and dead roots” (Sollins et al., 1996, page 66). This means that the driving force behind the formation of organic matter is the addition of carbon to soils and the stimulation of the microbial activity (Rees et al., 2005). Organic material in soils can be simple monomers, organic acids or mixtures of complex biopolymers aggregated together in form of cellular debris and can vary according to its decomposition from unaltered structures to highly decomposed material (Baldock and Skjemstad, 2000). Soil organic matter has a high water retention, a high cation exchange capacity, the ability to retain nutrients and to chelate and form complex ions, maintain biodiversity by providing food and habitat for soil animals and microorganisms (Karami et al., 2012). Different SOM pools in soil contribute differently to the various functions mentioned above (Baldock and Skjemstad, 2000).

Content of organic matter in soil is mainly influenced by particle size distribution, climate, land use (Ellerbrock and Kaiser, 2005) and by the chemical and physical properties of the parent substrate (Vlček et al., 2011).

Studies suggest that SOM cannot be formed unlimited if continuous organic material is added to the soil because a soil carbon saturation level limits the potential to store added carbon (Six et al., 2002). The chemical and physical properties of the soil matrix controls the decomposition of SOM and has only a finite and unique capacity to stabilise SOM (Baldock and Skjemstad, 2000). A study by Gulde et al. (2008) concluded that additional carbon input after the saturation of the mineral soil fraction leads only to an accumulation in the labile SOM pool which can be mineralized by the soil fauna.

2.3.1. The influence of land use on soil organic matter

Soil structure and SOM are extremely sensitive to land use management (Blanco- Canqui and Lal, 2004). The type of land use affects the amount and quality of litter input, its decomposition rates and the stabilisation processes (see Figure 3). Increased organic matter input to soil trough management practices enhances soil aggregation to a certain extent (Gulde et al., 2008). Microaggregation is not as sensitive to land use and cultivation practices as macroaggregation (John et al. 2005). It is assumed that the aggregates <20 µm are almost not affected by cultivation techniques or land use (Hassink, 1997).

Balesdent (1998) observed that the SOM content after 30 years of cultivation can get reduced by more than 70 % by ploughing. The turnover of soil organic carbon in the cropland can be 8 times higher than on forest sites due to inorganic fertilisation products that increase microbial activity due to higher nutrient availability and the negative influence of tillage on physical protection of SOM (Balesdent, 1998).

Land use management can however have long- lasting effects on quantity and quality of soil organic matter as it was exampled with a long- term field experiment since the 1950s by Gerzabek et al. (2006).

Forests have a positive influence on soil aggregation and there are many studies available dealing with different tree species on carbon fluxes in soils (Blanco- Canqui and Lal, 2004).

2.3.2. Soil organic matter in subsoil

The subsoil receives more and more attention for the storage and stabilisation of organic carbon in soils. One difficulty about studies in subsoil is that underlying processes for SOM storage are not identical in all horizons and therefore subsoil does not respond to changes of conditions in the same way like topsoil (Salome et al., 2010). A study by Fontaine et al. (2007) showed that decomposition of SOM in subsoil is strongly reduced. Its chemical composition does however not change markedly with depth what let's assume that stability of SOC in deep soil horizons is not caused by its chemical structure or a limitation of energy but, mainly due to physical protection. Other studies suggest that compared to the topsoil, subsoil organic matter is enriched in microbial- derived C compounds and depleted in energy rich plant material (Rumpel and Kögel-Knabner, 2011). It is stated that the main stabilisation mechanisms in lower horizons can be related to the mineral phase and to protection by the spatial separation of SOM, microorganisms and extracellular enzyme activity (Rumpel and Kögel- Knabner, 2011).

2.3.3. Stabilisation mechanisms of organic matter in soils

Very general, SOM stability is a term for how easy carbon and nitrogen in SOM is mineralized (Plante et al., 2011) or for the decrease of SOM by respiration (Sollins et al., 1996). Soil organic matter stability is not just a function of mineralization and chemical properties of the organic matter (Plante et al., 2011) but encompasses three main stabilisation mechanisms. These mechanisms are classified by different names physical protection/ chemical stabilisation/ biochemical stabilisation (Christensen, 1996); spatial inaccessibility/ interaction with surfaces and metal ions/ selective preservation (von Lützow et al., 2006); microaggregate- protected SOM/ silt- and clay protected SOM/ biochemically protected SOM (Six et al., 2002). The processes described in these mechanisms are however comparable.

The mechanisms of stabilisation lead to the formation of SOM pools according to their turnover time. The pools are separated in: active (turnover times > 10 years), intermediate (turnover times between 10 and 100 years) and passive pools (turnover times up to thousands of years; responsible for long term storage of SOM) (von Lützow et al., 2008). The labile pool contains, compared to the stable pool, very young SOM which is sensitive to land management and environmental conditions (Gulde et al., 2008).

SOM associated with clay sized microaggregates are mainly stabilised by physical protection within the aggregate and adsorption onto soil minerals. The relative importance of mechanisms are however still not clearly understood (Chenu and Plante et al., 2006).
Some other researchers suggest that several stabilisation mechanisms are operating simultaneously, but to a different degree (von Lützow et al., 2006). Organic matter in the passive pool may be stabilised by the spatial inaccessibility due to the occlusion in clay microstructures and due the formation of hydrophobic surfaces (von Lützow et al., 2008).

Von Lützow et al. (2008) tried to combine the stabilisation mechanisms, related them to different soil organic matter pools with their turnover times and created a conceptual model of organic matter stabilisation (see Figure 4). It shows that physical and chemical stabilisation mechanisms are responsible for the (more) stable intermediate and passive pool and that a biochemical stabilisation for the labile (active) pool and the most stable (passive) pool can be assumed.

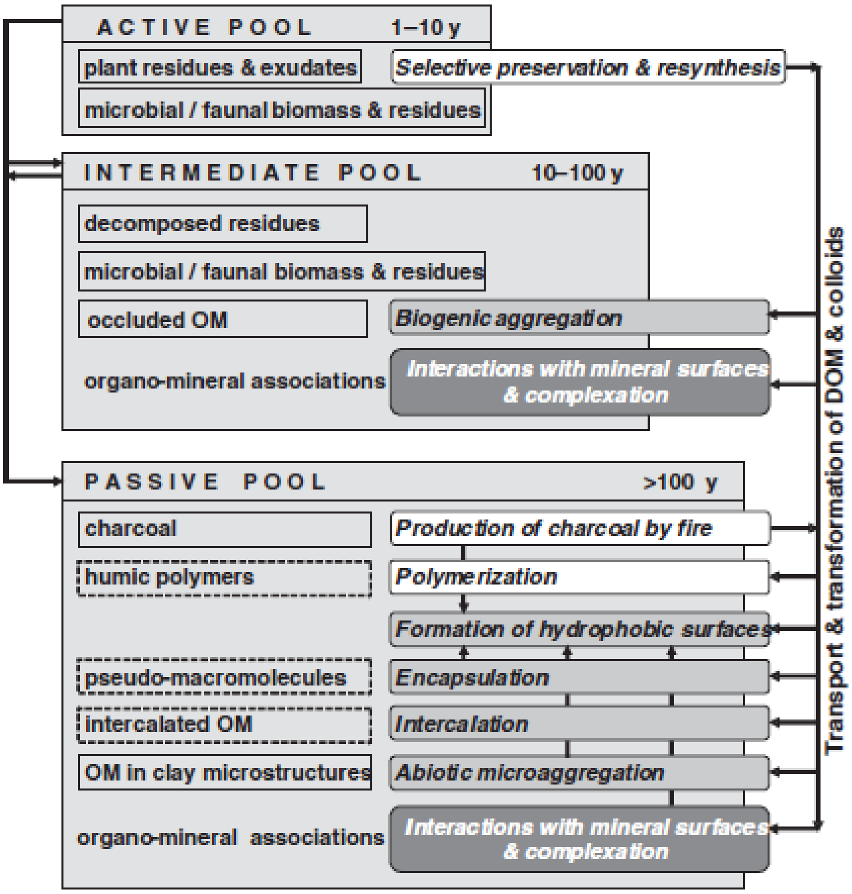


Figure 4: Conceptual model of SOM stabilisation

Pools within broken lines indicate postulated pools which existence is not verified by direct measurement.

□ = primary and secondary recalcitrance; (biochemical stabilisation)

▨ = spatial inaccessibility (Physical protection)

■ = organo- mineral interaction (Chemical/Physicochemical stabilisation)

Source: von Lützow et al.,2008

2.3.3.1. Physical protection of soil organic matter

Soil organic matter can be physically protected due to occlusion within soil aggregates (Six et al., 2002). Physical protection is also related to the ability of SOM to associate with silt and clay sized particles (Hassink, 1997) and is one of the main mechanisms responsible for the protection of organic matter related to the mineral phase (Chenu and Plante, 2006).

The influences of the processes responsible for protection of occluded organic material from decomposition are (von Lützow et al. 2006):

- reduced access for the microorganisms and their enzymes, which control further food web interactions;
- reduced diffusion of enzymes into the intra-aggregate space;
- restricted aerobic decomposition due to reduced diffusion of oxygen.

At the microstructure level less than 20 µm occlusion of SOM also occurs by abiotic mechanisms such as the formation of networks of Fe- and Al-oxides or hydroxides (von Lützow et al., 2006).

The limited microbial turnover in microaggregates is caused by the inaccessibility/ inactivation of mineral mesopores for extracellular enzymes in pore networks and lead to a protection of SOM against decomposition (Rabbi et al., 2010). Rabbi et al. (2010) explained that in those pores accessible to exo- enzymes, SOM is not decomposed because it is physiologically not profitable due to the tortuosity of the pore network. Beside the pore size exclusion, water filled porosity is a reason for the inaccessibility of substrates to microbes within aggregates (Six et al., 2002).

Some authors describe the physical protection mechanism as most important process according to SOM in clay sized microaggregates. Six et al. (2002) however proposed that chemical stabilisation is the most important factor for preservation of OM related to <2 µm sized aggregates because physical protection mainly occurs in 50- 250 µm aggregates.

2.3.3.2. Chemical/ Physico- chemical stabilisation

This stabilisation mechanism describes chemical or physicochemical binding between SOM and soil minerals (Six et al., 2002). Physical inaccessibility and the interaction with the mineral surfaces are dependent on the presence of multivalent cations, mineral surfaces capable of adsorbing organic substances and the architecture of the soil matrix (Baldock and Skjemstad, 2000).

The large surface area and charged surfaces of clay particles are responsible for different types of organic matter (from simple organic acids to complex bio-macromolecules) being adsorbed to clay particles (Rabbi et al., 2010). The adsorbed small molecules are unavailable to microorganisms unless they are desorbed and transported into the cell (von Lützow et al., 2006). Three main mechanisms are responsible for the interaction of SOM with soil mineral surfaces: ligand exchange, polyvalent cation bridges, and weak interactions (von Lüzow et al., 2006).

It is not clear if organic matter is distributed across the whole clay surface in a single layer or if there is a patchy distribution of organic matter on clay (Rabbi et al., 2010). Different types of clay however play an important role due to their substantial differences in CEC and specific surface area and their different involvement in mechanisms of aggregation (Six et al., 2002). Table 2 presents the different specific surface areas of some minerals.

Table 2: Specific surface area for clay minerals
Source: Schachtschabel et al., 1998

Mineral	Specific surface area [$m^2\ g^{-1}$]
Smectite and Vermiculite	600- 800
Illite	50- 200
Kaolinte	10- 150
Allophane and Imogolite	700- 1100
Goethite and Hematite	50- 150
Ferrihydrite	300- 400

The tetrahedral sheet of 2:1 and 1:1 phyllosilicates or neutral siloxane surfaces with no isomorphous substitution do not strongly participate in reactions compared to permanent charged sites within tetrahedral sheets (Rabbi et al., 2010).

Kaiser and Guggenberger (2003) did a study about the relationship of soil mineralogy, its surface area and SOM sorption. The study showed that sorption of SOM preferentially occurs at reactive sites in or at the mouth of micropores in early stages of SOM sorption. Less reactive sites sorbed more and more SOM as the loading increased. It was also explained that small amounts of organic matter sorbed in subsoil is efficiently preserved because the first molecules sorbed are the best stabilized (Kaiser and Guggenberger, 2003).

2.3.3.3. Biochemical stabilisation

Biochemical stabilisation of SOM happens due to chemical complexing processes and chemical composition e.g. recalcitrant compounds such as lignin and polyphenols (Six et al., 2002). Plant residues are composed of organic components: polysaccharides (starch, cellulose, hemicellulose and pectin; 50–60%), lignin (15–20%), and also proteins, polyphenols (e.g. tannins), chlorophyll, cutin and suberin, lipids and waxes (10–20%) (von Lützow et al., 2006). These components are differently biodegradable due to their structural composition.

Polymers (e.g. polysaccharides, proteins) have turnover times of some weeks while simple monomers (glucose and amino acids) show turnover times within hours or days (von Lützow et al., 2006). It seems that the biochemical stabilisation of plant residues is mainly relevant during the initial phases of litter decomposition (von Lützow et al., 2006). A large part of the stable OM in soils is composed of microbially and faunally derived compounds (von Lützow et al., 2006). There are indications for the apparent stabilisation of labile compounds, produced by microbial resynthesis and biomass recycling, because old OM contains large amounts of microbial polysaccharides and proteins but little is known about the involved mechanisms (von Lützow et al., 2006). The common assumption that functional groups like aromates are more resistant to decomposition and therefore have very long turnover times whereas labile components like carbohydrates have short turnover seems according to Kleber et al. (2011) not always to be true and also von Lützow et al. (2006) reported that chemical structure of organic molecules by itself is not sufficient to account for the extreme variation of soil OM in terms of age and turnover times. Kleber et al. (2011) suggested that organic matter turnover is more a function of microbial ecology and the physical and chemical stabilisation of SOM instead of its molecular structure.

2.4. Soil organic matter in particle size fractions

Macromolecule structures usually present most of organic matter in soils but cannot be investigated at a molecular level without degradative step (Kögel- Knabner, 2000) and so it is common to study the nature and distribution of SOM among special particle sizes (Moni et al., 2010). As already mentioned, clay fractions consist of the intermediate and passive pool, studies however showed that a higher allocation of SOC in small particles does not always cause longer turnover times (von Lützow et al., 2007). These slower turnover rates in the clay sized fractions can be explained by a combination of all stabilisation mechanisms at once (von Lützow et al., 2007).

This work analyses the clay sized microaggregates. Chenu and Plante (2006) showed that <2µm particles are micrometer sized microaggregates where organic matter is encrusted by minerals or coated minerals and that true primary organo- mineral complexes do not correspond to reality.

Various fractionation techniques have been developed. An absolute size distribution for a given soil sample does not exist (Stemmer et al., 1998). The choice of the fractionation procedure is however a crucial choice as different procedures provide different fractions and different impacts on soil properties.

2.4.1. Fractionation procedures

The review “SOM fractionation methods: Relevance to functional pools and to stabilization mechanisms” (von Lützow et al. 2007) can be recommended for a detailed description of fractionation schemes relating to soil organic matter analysis. Table 3 lists the available fractionation methods.

Fractionation procedures dissociate soil into its primary particles usually accomplished via chemical dispersion or physical techniques (Moni et al., 2010).

Chemical fractionation procedures extract SOM in aqueous solutions (with and without electrolytes), in organic solvents, on the hydrolysability of SOM with water and acids and the resistance of SOM to oxidation or by destroying different mineral phases (von Lützow et al., 2007). Chemical dispersions commonly determine the texture of soil by using hexametaphosphate (HMP) and overnight shaking after destruction of SOM by H_2O_2 oxidation (Moni et al., 2010). A positive aspect about chemical extraction is that they provide purely organic fractions (von Lützow et al., 2007). The use of chemical dispersants (HMP or sodium carbonate) without organic matter removal as first step, is not adequate for the dispersion of very stable micro- aggregates because they can solubilise organic matter, change its chemistry and physicochemical behaviour, and these chemicals are less dispersant than the use of ultrasonic procedures (Moni et al., 2010).

Table 3: Available chemical and physical fractionation methods

Source: Modified after von Lützow et al., 2007

Chemical Fractionation	● Extraction procedures (Dissolved organic matter, soil microbial biomass, fulvic/humic acid and humin fraction, organic solvents) ● Hydrolysis of OM (Hot water, acids like HCl/ H_2SO_4) ● Oxidation of OM ($KMnO_4$, UV photooxidation, H_2O_2, disodium peroxodisulfate, sodium hypochlorite) ● Destruction of mineral phase (Hydrofluoric acid, dithionite and oxalate)
Physical fractionation	● Aggregate fractionation ● Particle size fractionation ● Density fractionation ● High- gradient magnetic separation (HGMS)

Physical methods are based on the theory that the association of soil particles and their spatial arrangement play a key role in soil organic matter dynamics due to its bioaccessibility (which is a prerequisite for decomposition) (von Lützow et al., 2007).

Physical fractionation techniques are increasingly used to study the turnover of SOM because they are chemically less destructive than chemical fractionation procedures and their results are more directly related to the real structure and function of SOM (Christensen, 1992). Particle size and/or density fractionation helps to quantify SOM pools with different stability and allows combining these results with the architecture and function of a soil (Müller et al., 2011).

There exists no single fractionation procedure, but physical fractionation methods mostly rely on different types of ultrasonic treatments for dispersion (Kögel- Knabner, 2000). Sonication can maintain the physicochemical integrity of the SOM and can completely disperse soil aggregates up to 2 µm with an appropriate energy level (Schmidt et al., 1999)

The basis for the particle size fractionation method is the assumption that the characteristic of organic matter in different sized classes are important for the regulation of OM turnover and that SOM is associated with different sized mineral particles (Christensen, 2001). Sand fractions are dominated by quartz particles causing weak binding effects to SOM whereas clay- sized particles (e.g. sesquioxides, layer silicates) provide large reactive sites and play an important role in carbon storage and SOM stabilisation (von Lützow et al., 2007).

2.5. Characterisation of soil organic matter

A detailed review of the current available and most used analytical techniques to receive structural information of soil organic matter is given by the paper "Analytical approaches for characterizing soil organic matter" by Kögel- Knabner et al. (2000).

^{13}C and ^{15}N NMR are at the moment widely used for analysing organic matter composition in soil. Kögel- Knabner (2000) described that the intensity of an NMR signal is proportional to the concentration of nuclei what creates the signal. Different chemical shifts give information of the alkyl C, O- alkyl C, aromatic C and carboxyl C content. The use of NMR is limited in soils with low carbon content due to sensitivity problems and in soils with high concentration of paramagnetic compounds (Fe, Cu) and carbonates.

This method is very useful for further analysis. Compared with the data of a STA the ^{13}C NMR could provide a very detailed picture of SOM in the analysed clay sized microaggregates.

In recent years Simultaneous Thermal Analysis (STA) were used increasingly to analyse SOM and its thermal stability (Plante et al., 2009). Thermal Analysis can characterise chemical changes of soil organic matter and can be used to compare the proportions of active/labile and more stable components (Lopez- Capel et al., 2005). This is done by a continuously measurement of the weight loss in the temperature range of 200- 600 °C. Organic matter compounds have different and contrasting thermal stability what leads to different exothermic reaction from its decomposition (Lopez- Capel et al., 2005).

Studies showed that thermal analysis provide suitable and sufficient data of soil organic matter and its stability but cannot replace chemical analysis (Plante et al., 2009). Therefore, coupling techniques like Evolved Gas Analysis (EGA) by FT-IR, gas chromatography (GC), mass spectrometry (MS), isotope- ratio mass spectrometry (IRMS) or/and elemental analysis are common (Plante et al., 2009).

De la Rosa et al., (2008) used a thermogravimetry coupled with pyrolysis- gas chromatography/mass spectrometry (Py- GC/MS), a IRMS, and a solid state ^{13}C NMR. The study showed a strong positive correlation between the labile SOM pool (Exo1) and proportion of alkyl C determined by NMR, a positive correlations between Exo2 (more stable pool) and aromatic species, and Exo 3 is positively correlated with amounts of ketones and oxygenated aromatic functional groups.

Studies like this, or reports which showed that soils have a different thermal stability according to their horizon or land use management (Plante et al., 2009) promised to yield useful data with this measurement. It is more difficult to yield information of the influence of land use on organo- mineral fractions than on the light fraction due to the thermal composition of clay minerals (Lopez- Capel et al., 2005). According to Plante et al. (2009), most clay minerals feature endothermic peaks at temperatures fewer than 200°C due to loss of water or at temperatures above 600°C due to dehydroxylation. Some clay minerals show a thermal reaction in the temperature region between 200- 600°C but their contribution is relatively small compared to that of SOM on an equivalent mass basis (Plante et al., 2011).

Another advantage of the use of STA is that high carbonate content does not disturb the data received from the STA because carbonates decompose at temperatures exceeding 600°C (Lopez- Capel et al., 2005). The received data from the STA in this study seems therefore reliable and not influenced by undesired factors.

3. MATERIAL AND METHODS

3.1. Study area

A previous study at the University for Natural Resources and Life Sciences by Lair et al. (2007) showed that the age of soil varies enormous within a small area in the Marchfeld. This chronosequence study was the starting point for this thesis. The experiment is part of a European programme called "SoilTrEC". The main aim of the SoilTreC programme is to "*address the priority research areas identified in the European Union Soil Thematic Strategy and to provide leadership for a global network of Critical Zone Observatories (CZO) committed to soil research*" (SoilTrEC, s.d.).
All soils were collected in the Marchfeld region in spring 2011 and were chosen according to its age and land use management.

The study area is situated in the Marchfeld (Figure 5) which belongs to the territory of Lower Austria in the eastern part of Austria. A part of the study area is located within the "Nationalpark Donau- Auen" and strongly influenced by the Danube River. Flood events bring differently textured sediments depending on local topography and flow conditions (see chapter 4.1.3.) (Lair et al., 2009, a)

Morphologically seen, the Marchfeld can be divided into a terrace called "Younger part of today's valley" (=alluvium) (soil samples 1, 2, 3) and "Higher and older part of today's valley floor" (=Marchfeld fluvial terrace) where also a set of samples (soil samples 4, 5, 6) were taken (Lair et al., 2009, b). The formation of terrace staircases is caused by riverbed incision during interglacial warm periods (Lair et al., 2009, a).
The study area and the Danube River in this area are strongly influenced by mankind. From 1870 to 1875, a river regulation was created who caused the present main channel and from 1882 to 1905 a protection dike was build which disconnected the area outside the dike form

the Danube (Lair et al., 2009, b). Site 3, 4, 5 and 6 are affected by this dike and do not undergo recurrent flood events since the construction.

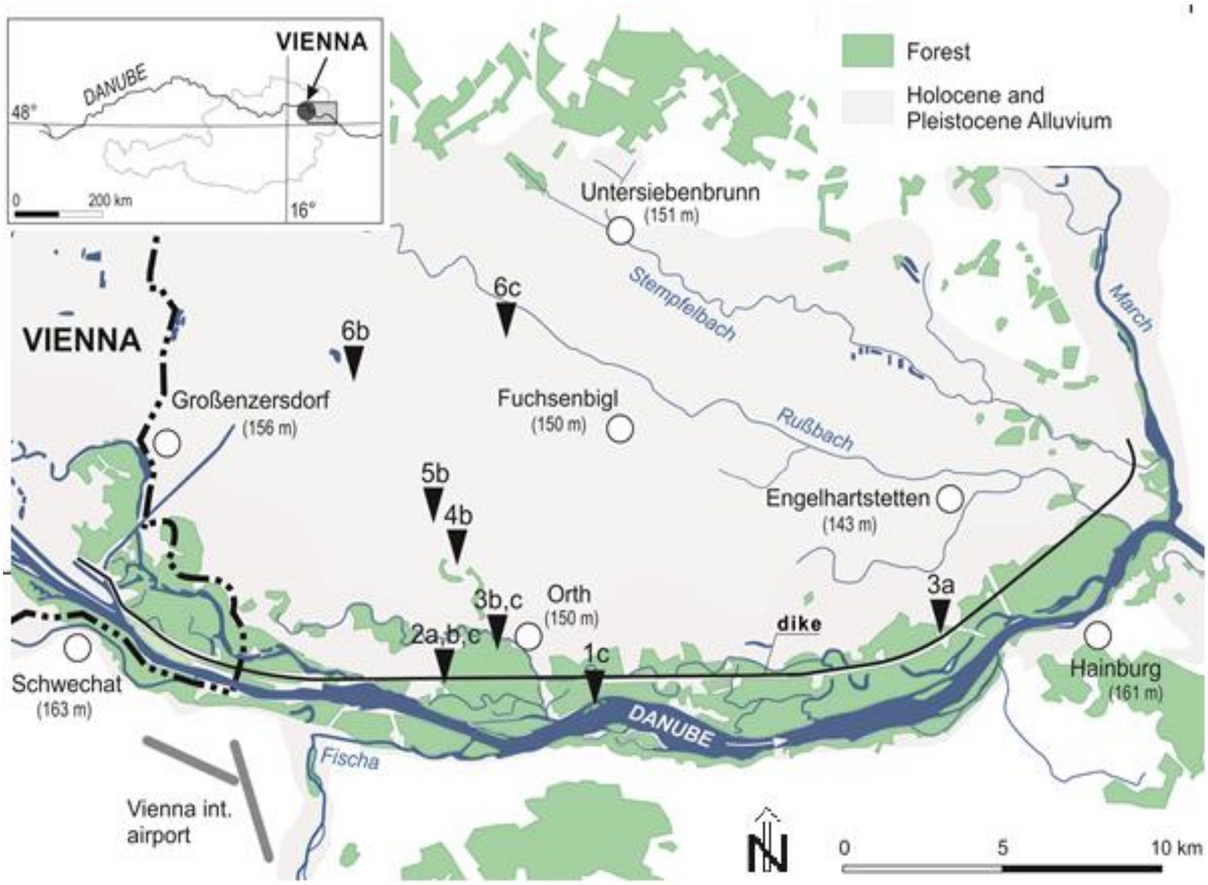


Figure 5: Study area in the Marchfeld, east of Vienna/Austria

Triangles indicate the sampling sites following a substrate age gradient

The continental climate in the area shows a mean annual temperature of ~ 9°C and a mean annual precipitation of about 550 mm. The mean annual potential evapotranspiration of 570 mm leads to a negative water balance (especially in the summer season) (Lair et al., 2009 b).

The age of the individual soil horizons was analysed with a chronofunction, relating Fe oxide crystallinity in the soils (Fe_o/Fe_d) to soil age, measured with ^{137}Cs and optically stimulated luminescence (Lair et al., 2007).

The history of land use management in the Marchfeld can be exactly retraced till the late 18th century due to an intense study by Hartmann (2003). The first settlement in this area was very spare in the Neolithic period and increased from the Copper Age to Iron Age (Hartmann, 2003). At the time of the Roman Empire settlement disappeared and it is known that until the 11th century the Marchfeld had no clear settlement (Hartmann, 2003). Therefore it can be assumed since the Middle Ages farm land was established in the Marchfeld.

3.2. Soil description

The soils developed on Danube sediments, are classified as Fluvisols (sites 1, 2 and 3) and show a progressing development with age and further distance of the Danube to Chernozems (sites 4, 5 and 6) (Lair et al., 2007; Gerzabek et al., 2010). The clay amount ranges from 9.7- 21.8 % in the A horizon and 6.9- 23.6 % in the AC horizon (detailed clay amounts see Appendix) and showed little variation along the whole chronosequence.

Table 4: Site description and average soil properties

Site	land use	Soil age [yrs]	A horizon depth [cm]	A horizon Clay Fraction [%]	A horizon pH (H_2O)	AC horizon depth [cm]	AC horizon Clay Fraction [%]	AC horizon pH (H_2O)
1c	forest	10	0-10	9.76	7.58	40-45	6.98	7.93
2a	grassland	80	0-10	12.23	7.62	15-25	13.80	7.66
2b	cropland	80	0-10	14.46	7.86	25-35	16.34	7.95
2c	forest	80	0-10	12.59	7.58	20-30	16.22	7.92
3a	grassland	350	0-10	13.41	7.51	15-30	13.91	7.95
3b	cropland	350	0-10	21.84	7.94	35-45	19.70	8.07
3c	forest	350	0-10	16.41	7.62	35-45	17.06	8.03
4b	cropland	2600	0-10	18.89	7.96	40-45	23.63	8.41
5b	cropland	2300	0-10	16.86	8.34	75-90*	14.70	8.46
6b	cropland	4000	0-10	20.66	8.06	50-60	14.73	8.47
6c	forest	4500	0-10	19.14	7.89	50-60	12.41	8.66

*Soil profile is anthropogenic influenced

The soil pH does not change markedly and stays on all sites in the slightly alkali group which is getting more intense with increasing age (see Table 4). Especially old subsoils contain a lot of carbonates (up to almost 70 %). The soils have a thin A horizon in early stages of soil development which is increasing with time. The oldest soils show the deepest A horizons which go down to a depth of 60 cm.

Young site:

Site 1 is the reference site with a recently developed soil. The site is on an island in the Danube River and the topsoil was deposited during the high flood in 2002. The river regulation in the 1870s caused formation of islands and a higher flow velocity in the main channel what causes a lower deposition of clay sized material (Lair et al., 2009, b). The AC horizon at site 1 can be seen as a starting point of soil formation.

Medium aged sites:

Site 2 and site 3 are of young to medium age. At these sites it was possible to get material from sites used as forest, grassland and cropland in a similar age group. This allows a comparison of the influence of different land uses and gives information if the age or the land use is the driving factor for soil organic matter storage.

Site 3 is located outside the artificial dike. Therefore this site has not been influenced by the river dynamic and addition of fresh material by the Danube River for about 100 years.

Old Sites:

Site 4- 6 are the oldest soils detected so far in the Marchfeld. Site 4 and 5 are around 2600 and 2300 years old. The deep AC horizon at site 5 should be neglected because it can be assumed that the horizons were mixed at nearby construction works. Both sites are used as cropland.

Site 6 is most far away from the Danube (9 km) and the soils are the oldest in the region. The soils differ especially by their dark colour to the soils of other sites and their high carbonate content in the AC horizon. The exact soil age was not measured yet but it can be considered between 4000 to 10000 years. According to the Fe_o/Fe_d ratio a soil age of 4000-5000 years was estimated for this study (Lair et al., 2011, pers. communication).

3.3. Soil sampling

The soil sampling campaign was performed in April 2011 on the A and AC horizon from four forest sites, two grassland and five cropland sites (see Table 4 and Figure 5).

An 8 cm core drill with a core height of 15 cm was used at each study site for sampling. The depth of the AC horizon was chosen according to soil colour and structure at each profile and reaches a depth of 60 cm at the oldest soils. It seems that Chernozem soils in the Marchfeld do not show a deeper A horizon than down to 60 cm.

Three replicates evenly distributed in a triangle over each site were sampled. The fresh core samples were crumbled by hand into a 10 mm sieve in the field and stored in plastic bags in a cool (4°C) and dark room.

3.4. Sample Preparation

To gain the clay- sized aggregates, a particle size fractionation method (see Figure 6) was chosen according to Monrozier et al. (1991) and Stemmer et al. (1998) in this study.

Ultrasonic dispersion is able to disrupt soil aggregates into smaller aggregates and particles without chemical contamination (Mentler et al., 2004). High energy sonication might introduce uncertainties concerning redistribution of physically unprotected SOM or destruction of intact molecules and formation of artifacts (Amelung and Zech, 1999; Schmidt et al., 1999). A low- energy sonication was therefore chosen to yield a particle size distribution close to the natural one without disrupting stable microaggregates (Stemmer et al., 1998).

Field moist soil (20 gram) was placed into a plastic beaker with 200 ml deionized water. This was done six times for each soil to receive approximately 100 gram equivalent treated amount of dry soil. The ultrasonication was performed using a Bandelin Electronic UW2200. The device was set to 55 Watt output energy for 200 seconds. The tip had a cylindrical shape and was plunged 15 mm into the suspension (see Figure 8). The solution was stirred with a magnetic stirring device during the ultrasonic treatment to obtain a homogenous energy absorption by the soil particles in the solution.

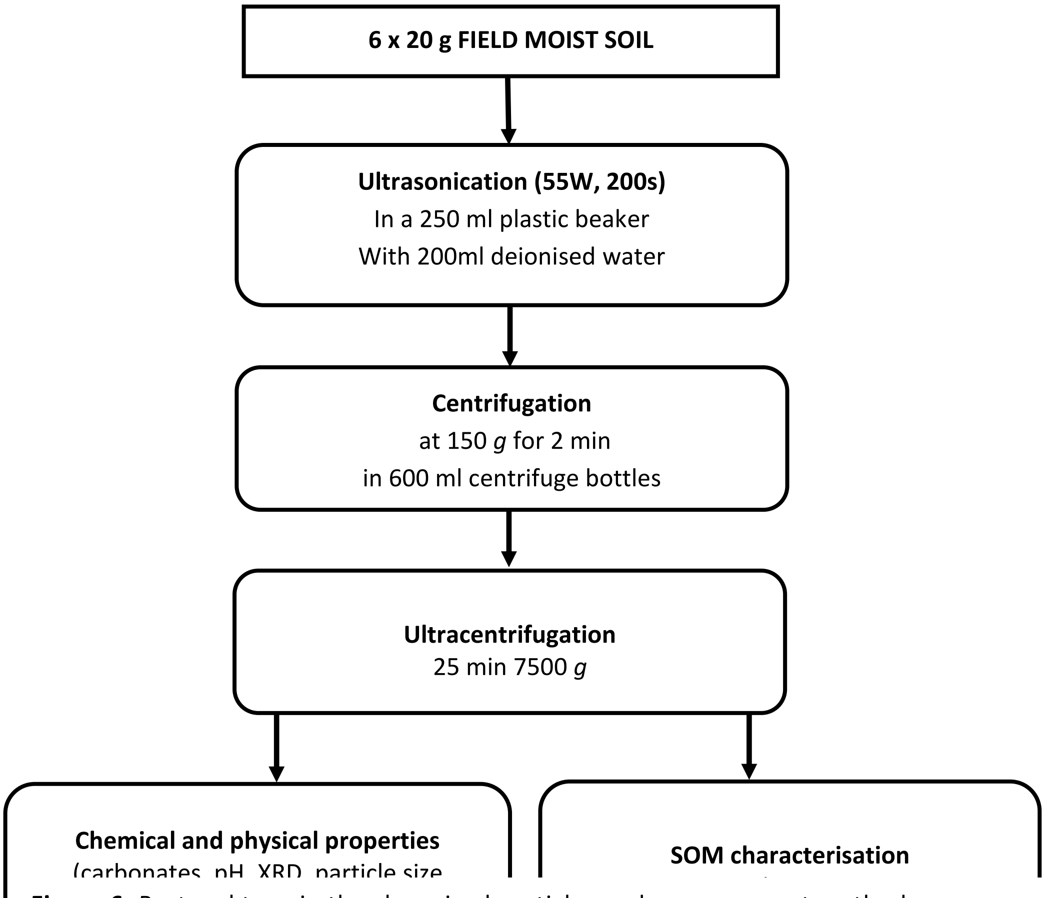


Figure 6: Protocol to gain the clay- sized particles and measurement methods

To calculate the power output, the cavitational energy applied by ultrasonication was assessed by calorimetrical calibration after Schmidt et al. (1999) and Schomakers et al. (2011). The ultrasonic probe was inserted in water and the increase of water temperature during a specific time period was measured. The change of thermal energy of the water is dependent on ultrasonic vibrations, the heat exchange with ultrasonic probe, beaker and laboratory air (Schomakers et al., 2011). This measurement was repeated until the power output reached the wished energy of 55 Watt (Figure 7 presents the used equation to calculate the energy output).

$$P=m_w c_w \Delta T/\Delta t$$

P= Power

c_w*= specific heat capacity of water (4,18 J* g^{-1} K^{-1}*)*

Δt= sonication time

m_w*= mass of water*

ΔT= Difference in Temperature

H= energy loss by conduction

Figure 7: Calculation of ultrasonic power output

Source: Schmidt et al., 1999 and Schomakers et al., 2011

Some soil samples contained earthworm exudates. Tests with high energy ultrasonication showed that these are very stable and do not get destroyed. Due to this special stability the exudates were collected. The water- soil suspensions of each sample was put through a 2 mm sieve after ultrasonication to separate the rain worm exudates for possible further analysis.

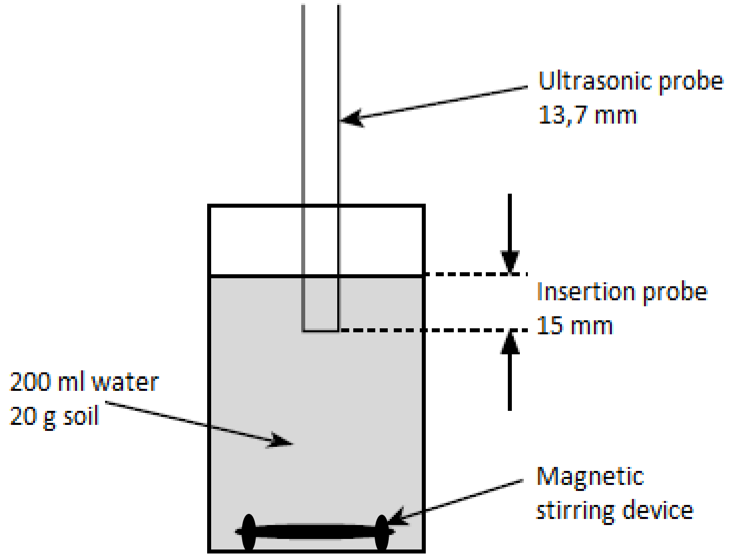


Figure 8: Principle of the probe- type ultrasonic dispersion experiments
Source: slightly modified after Mentler et al., 2004

To separate the clay fraction (< 2 µm) from the bulk soil, the suspensions were filled into a 600 ml centrifuge bottle after ultrasonication and centrifuged at 150 *g* (834 rpm) for 2 minutes with maximal starting and stopping speed.

The clay fraction was gained by sucking up the supernatant in the centrifuge bottles with a hydraulic water pump. To remove particles smaller than 0.1 µm, the suspension was finally ultracentrifuged in 250 ml metal cups at 10000 *g* (7400 rpm) for 25 minutes. The supernatant was removed and the pellet gained, freeze dried, milled in an agate mill and stored for subsequent analysis.

3.5. Analysis of soil properties and soil organic matter

3.5.1. Basic soil characterisation

Soil pH of the bulk soil was determined in deionised water (soil: solution ratio 1: 5) and an overnight reaction without shaking. The measurement was carried out according to the guideline ÖNORM L 1083- 99.

A particle size distribution of the clay sized microaggregates was measured on some samples. Prior to the analysis, the organic matter was removed from the soil with 30% hydrogen peroxide. When the organic matter was gone, the solution was cooked to remove the hydrogen peroxide and afterwards the clean soil solution was analysed using an X- Ray sedigraph (Micromeritics SediGraph 5000).

The carbonate content of the mass of the soil (m_s) was calculated with the released CO_2 volume in the calcimeter according to Scheibler instrument (V) the air pressure (p) and temperature (T) in the laboratory by following equation:

$$CaCO_3 = V*p*1{,}204*1{,}337/(T+273{,}2)*m_s*10$$

The total organic carbon and nitrogen contents were determined using an elemental analyser (Carlo Erba, Milano). The organic carbon (C_{org}) content was received by subtracting the inorganic carbon contents received from the total organic carbon content.

3.5.2. Simultaneous Thermal Analysis (STA)

The Simultaneous Thermal Analysis (STA) was performed using a Netzsch STA 409 PC and measured the continuous and simultaneous weight loss (TG).

Approximately 50 mg of sample was heated from 25°C to 600°C with a heating rate of 5°C min^{-1} and was analysed under an atmosphere of synthetic air (air flow: 50 mL min^{-1}).

The weight loss of the sample was normalised to the initial mass. The corresponding signals were exported to the Netzsch TA4 software for analysis as a function of temperature.

A STA detects all exothermic (sample temperature increases relative to reference) and endothermic (sample temperature decreases relative to reference) reactions as a function of temperature (Plante et al., 2009).The received data was presented as total weight loss (Exo_{tot}) in the temperature range between 190- 600°C. Exo_{tot} represents the thermal decomposition of organic constituents (Lopez- Capel et al., 2005) and represents the total SOM content [%] and allowed a calculation of SOM in g kg^{-1}. The different pools were calculated with Exo1, Exo2 and Exo3 proportional to the total SOM content. Lopez- Capel et al. (2006) suggested the ratio of labile: stable SOM can be calculated by the ratio of Exo1: Exo2+3.

4. RESULTS AND DISCUSSION

4.1. Changes of soil properties along the age gradient

4.1.1. Soil colour

Schaetzl and Anderson (2005) explained soil colour as the simplest method to receive general information of soil development, even if a detailed description is difficult because the colour is influenced by many parameters. The soil colour is a function of type and degree of its various coatings. A black or dark brown colour can be attributed to humus coatings, white to carbonates or a red/brown to iron minerals. To describe the colour of a soil accurately, soil samples have to be compared to standardized colour chips in the "Munsell Colour Charts".

The Munsell Colour Charts explains three elements (Schaetzl and Anderson, 2005):

- *hue*: chromatic compensation or wavelength of light; mainly influenced by mineralogy
- *value*: describes the darkness/ lightness or intensity of colours; low value= dark colour (influenced by C_{org} or wet soil), high value= light colour;
- *chroma*: purity, strength or greyness of a colour

Elliot (s. d.) observed that in some chronosequence studies, older soils show a redder colour than young. Redding cannot be used as a relative indicator for age because also other factors like site specific soil moisture influences the formation of different (hydr)oxides (Elliot, s.d.). Almost all our studied soils in the A horizons (except site 1) are in the yellow-red group "10YR" (see Figure 9). They do not show a clear reddening but generally the older soils are darker and more "pure" in colour. The youngest site on the island does not show a big colour difference between the A and AC horizon.

The soils in the AC horizon are brighter and situated in the more yellow group "2,5 Y" reflecting the colour of the parent material. The AC horizons of older soils have a higher "value" than the young soils. This means that they are brighter. A reason for the brighter subsoil at old sites can be the high carbonate content in the subsoil. The AC horizon at site 3A was chosen at 15-30 cm and is situated in the 10YR group. This shallow depth of the AC horizon could explain why the soil colour differs to others in the subsoil showing a pronounced soil development with depth (e.g. formation of different (hydr)oxides) from top to subsoil in the study area.

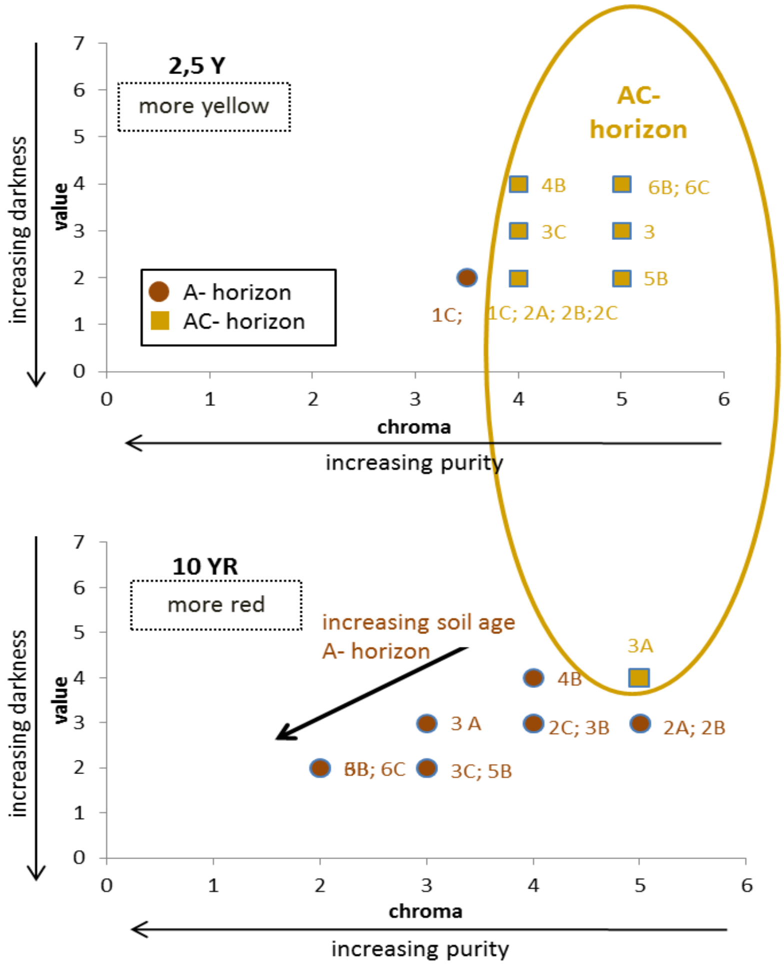


Figure 9: Munsell colour charts

4.1.2. *Clay fraction*

Lair et al. (2009) mentioned that in the study area, flood events cause differently textured sediments, depending on local topography and flow conditions. Small particles mainly accumulate in depressions and the soils in the older former floodplain show higher clay content than island sites (Lair et al., 2009). The clay content is however not only influenced by river flow regime. The deposition of clay particles in the study area (see Figure 10) shows that the clay content is quite constant with increasing distance from the Danube and independent of soil age. There is however a noticeable increase at study sites from 80 to 350 years. This can be explained due to anthropogenic influences. Chapter 3.1. already mentioned that in the 19th century a systematic river channelization and a dike was built in this study area. The study performed by Lair et al. (2009) mentions that since then a considerable reduction of erosion and deposition has occurred. It is reasonable that this is the main influencing parameter for the lower clay content in soils younger than 100 years. The clay content of the upper horizons do not differ remarkably to the subsoils (see Appendix 1).

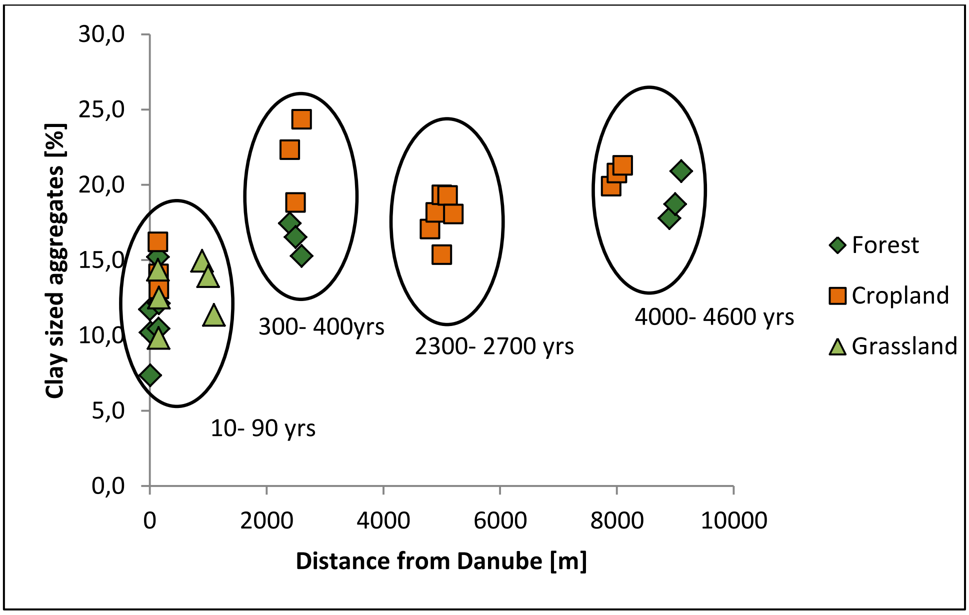


Figure 10: Clay sized aggregates in the A horizon dependent on the distance to the River Danube and soil age

A particle size analysis was carried out on the clay- sized microaggregates. This analysis showed that the received fraction is not bigger than 6 µm and more than 90 % of particles to be less than 2 µm. The distribution of the particles <6 µm is equal in all samples and there was no change detectable along the chronosequence or due to different land uses.

The mineralogical composition of the clay sized fraction was analysed with an X-ray diffraction (XRD). Our results showed no change of the clay mineral composition over time. This suggests that on these sites, the clay mineral type is not responsible for any changes of soil properties or organic matter composition along the chronosequence. Another study dealing with soil formation in an alpine glacier related to a chronosequence also showed only small changes in the clay mineralogy with increasing time and that significant changes of clay minerals only occur in late stages of soil development in an alpine area (Dümig et al., 2012).

As already mentioned above, some scientists propose that the amount of carbon sorbed by clay minerals is dependent on clay mineral type. Although different minerals bind SOM to a different intensity, this factor can be neglected in our study.

The main minerals in the studied soils in the chronosequence are calcite/dolomite, illite and feldspar.

4.1.3. pH and carbonates

The pH value in the bulk soil ranges from 7.4 to 8.7 (see Figure 11). This indicates an alkaline soil. Soil pH is one of the basic parameters influencing soil organic matter content, the formation of hydroxides and soil biota. The analysed soils have a high carbonate content which buffers the pH value. In the AC horizon carbonate content and pH increases (see Figure 11 and 12).

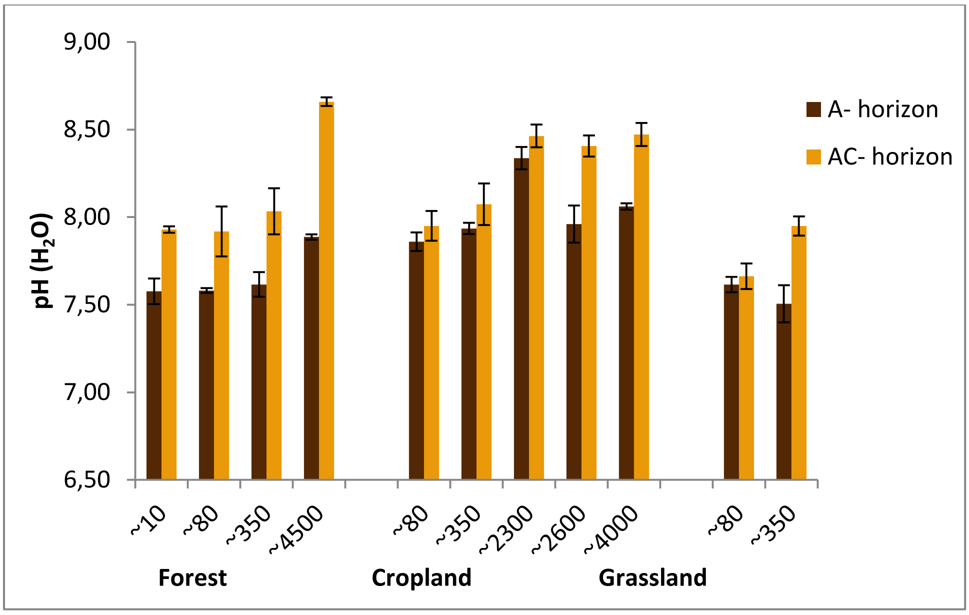


Figure 11: pH (H_2O) in the A and AC horizon oft the bulk soil

A comparison with carbonate or SOM content of the bulk soil (not with the clay sized microaggregates as it was measured) might show an even clearer correlation.

Forest and cropland sites (except the 4000 year old soil used as cropland) become more alkaline along the soil chronosequence. The A horizon does not show such a strong pH trend with time as the AC horizon (see Figure 11). The AC horizon under forest is from the beginning of soil formation more alkaline than the upper horizon which can be influenced by the River Danube. This difference is increasing with time. Comparing the soils according to their land use management the sites used as cropland show higher values than other soils in the same age group. Jones et al. (2002) explained that crop removal decreases SOM content and acidification and causes a higher pH in cultivated soils. Tillage causes a displacement of $CaCO_3$ from the subsoil to the upper soil horizon and also irrigation water containing higher amounts of reactive CA carbonates have probably increased the pH in our cropland topsoil.

Figure 12 illustrates the increasing carbonate content along the age gradient in the AC horizon and the more stable contents in the A horizon.

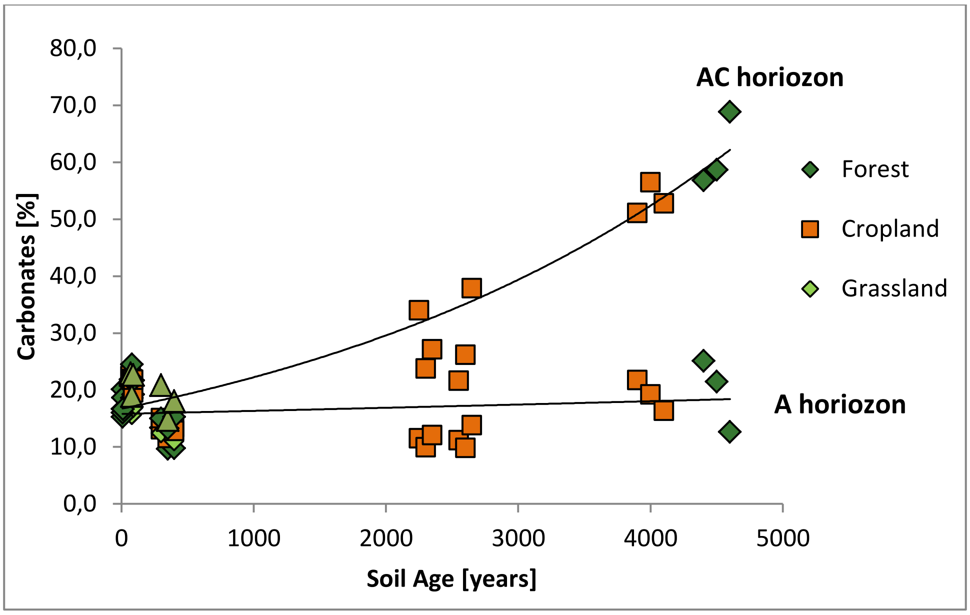


Figure 12: Carbonate content in soils along the chronosequence

At the beginning of soil formation (site1, ~10 years) carbonate content in the A horizon is slightly higher than in the AC horizon. After 80 years, the carbonate content in the subsoil is already higher than in the upper part of the soil. This leaching process from the top- to the subsoils is continuing with soil age and can be influenced by rain and groundwater and the activity of soil organisms (e.g. earthworms).

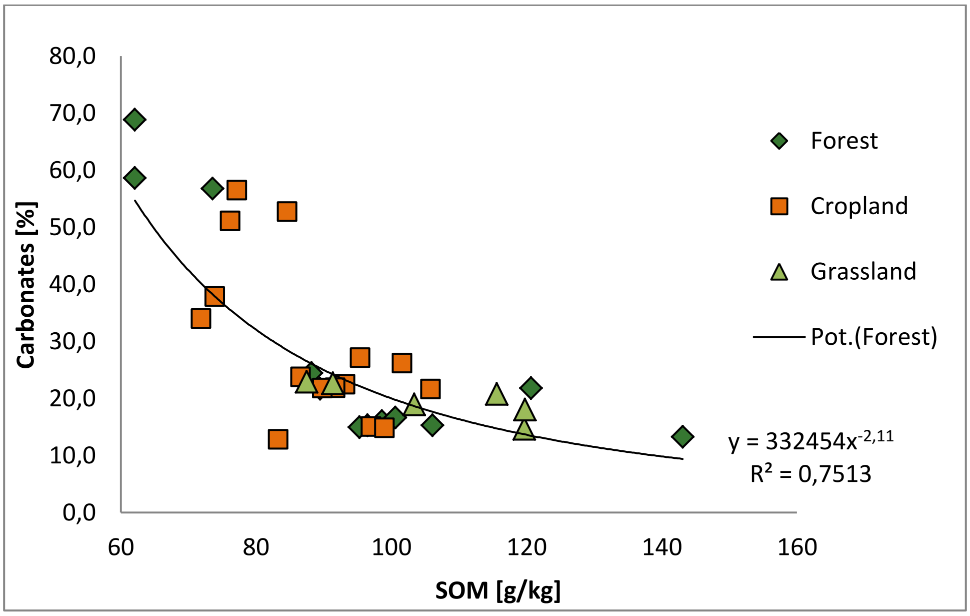


Figure 13: Relationship of carbonate content and SOM content in the AC horizon

Soils in the same age group, but different land- use management, have similar carbonate contents in the topsoil. This shows that management practices do not affect carbonate content and soil age is the main factor influencing $CaCO_3$ in the subsoil.

Some field and laboratory studies showed that high carbonate content in alkaline soil has positive influence on SOM stabilisation due to the complexation of organic matter with cations at high soil pH (Grünewald et al., 2000). Grünewald et al. (2000) mentioned also a negative influence of alkaline pH for SOM sorption/ stabilisation processes because Fe and Al oxides possess only small surface charge and can bind less negatively charged organic material under such conditions as under neutral soil conditions.

In this study, the AC horizon showed a decrease of SOM with increasing carbonate content (see Figure 13) which reflects the soil development with a relatively rapid accumulation of the carbonates and a slower accumulation of SOM in the AC horizons of the Chernozems.

4.2. Soil organic matter content

Soil organic matter content is increasing in the A horizon along the chronosequence (see Figure 14). The forest and grassland sites show a higher SOM content than cropland sites from the beginning of soil formation onwards. SOM is increasing very rapidly in the first 350 years. It seems that after that time period, SOM content reaches a steady state because in the next 4000 years SOM increases only slightly. This confirms the hypothesis and assumptions that the clay minerals are loaded very fast with SOM and then reach a point where they are saturated and are not able to bind more organic matter.

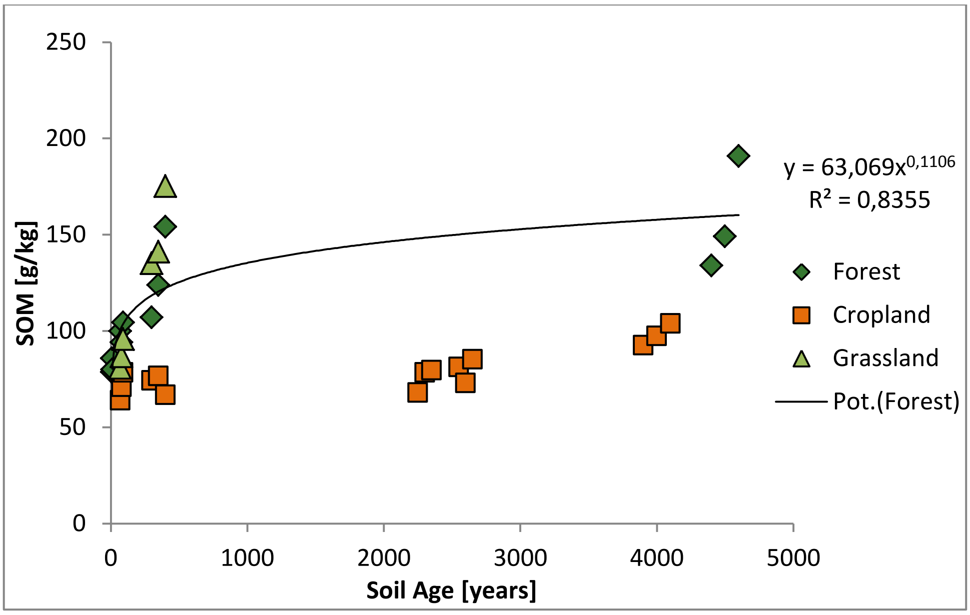


Figure 14: SOM content in the A horizon

Soils used for cropland behave different compared to soils with grassland and forest management. The cultivated sites contain less organic matter in all clay sized aggregates. A steep increase of SOM content in the first years of soil development is not detectable. The accumulation of SOM is very slow but, compared to other land uses, no equilibrium of storage can be found. An increase of SOM along the age gradient under cropping systems can be restricted by regular disturbances like tillage.

It has to be considered that SOM content was measured in the very small aggregates which are considered to be not very influenced by land use management. Hassink (1997) mentions that SOM in clay and silt particles are mainly affected by its soil texture. The input of organic material and cultivation has less influence on SOM content. Our samples do show an influence. It can however be assumed that the difference in the bulk soil is much higher and distinct than in the observed fraction.

The AC horizon has a different SOM distribution (see Figure 15). SOM content decreases constantly after 350 years of soil development or when the A horizon gets deeper than 45 cm along the chronosequence at all sites independent of their management.

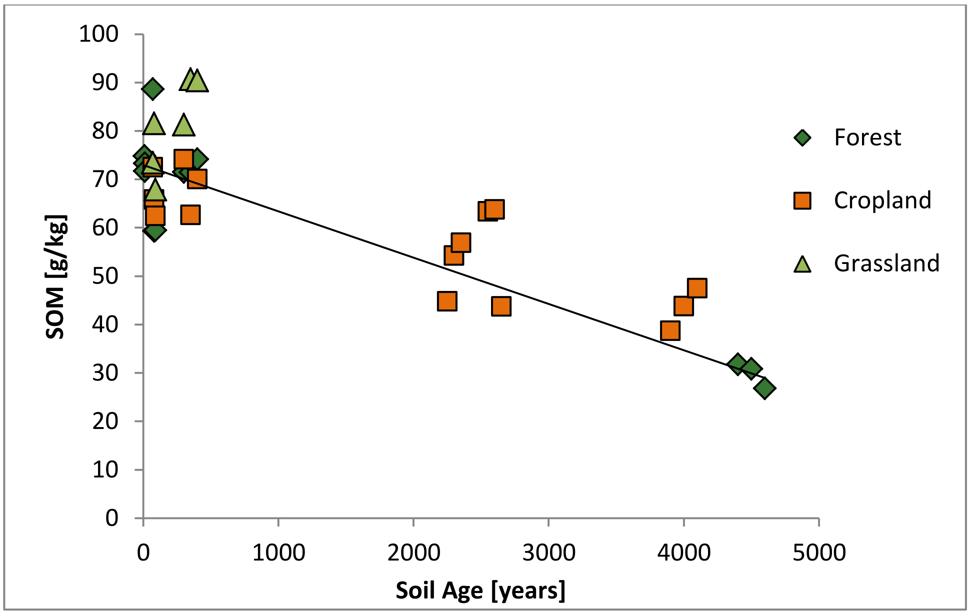


Figure 15: SOM content in the AC horizon

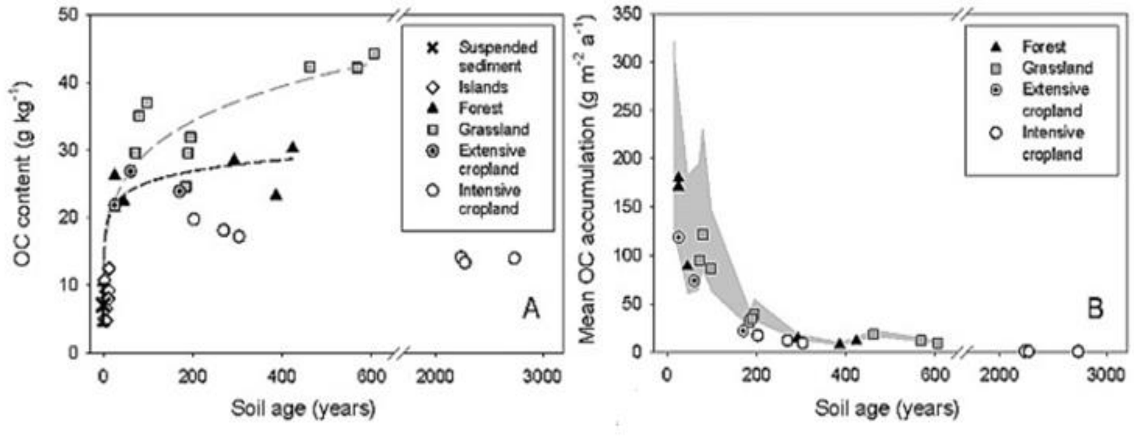
4.2.1. Organic carbon

Zehetner et al. (2009) did a study on bulk soils in the Marchfeld. The organic carbon content in grassland and forest sites, presented in Figure 15, increase strongly in the first 50 to 100 years. In the next 300 to 500 years a levelling off occurs. This is also reflected in the organic carbon accumulation rate. According to Zehetner et al. (2009) the mean organic carbon accumulation rate decreases exponentially in the topsoil (0-20 cm) soil with increasing soil age.

Figure 16: Mean organic carbon accumulation rates to 20cm depth at comparable study sites in the Marchfeld

Shaded area= uncertainties due to age estimation

Soure: Zehetner et al., 2009



The results of organic carbon in clay sized aggregates are similar to the bulk soil at our study site. The C_{org} content in the AC horizon at the 10 year old site is very similar to the parent substrate and can therefore be seen as initial organic carbon content. This let us assume that in the very short period in the first years of soil development, organic carbon is already accumulated to a quite high amount.

Root systems or animal activity can bring organic carbon to deeper layers where clay sized micro aggregates still have a high capacity to store organic matter.

SOC contents in the AC horizon are smaller than in the A horizon but the difference is increasing along the age gradient in all land uses (see Figure 17). At forest sites, the AC horizon at the 10 year old site contains proportional 37 g/kg and at the oldest site only 15 g/kg.

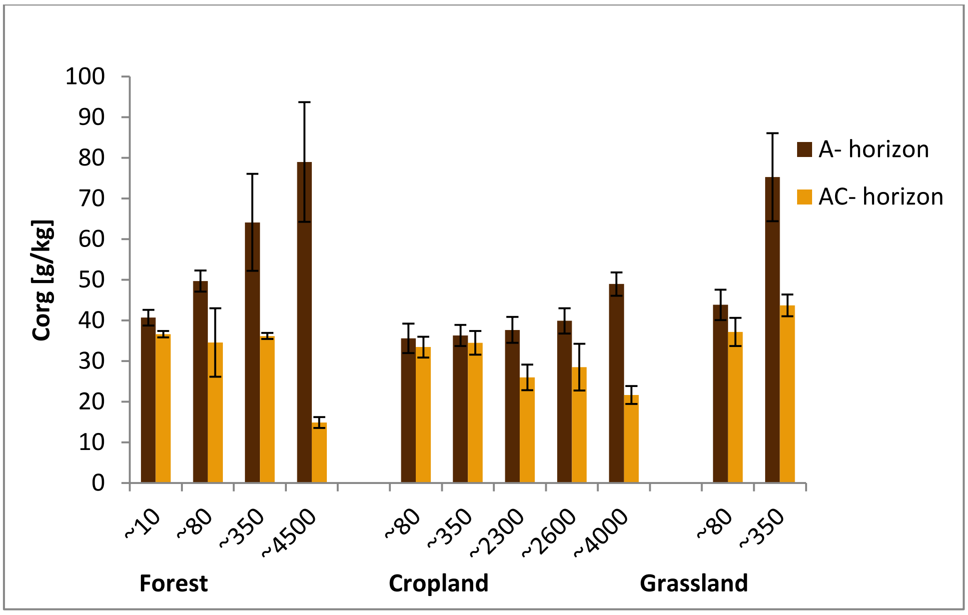


Figure 17: C_{org} content [g/kg] of A and AC horizon

4.2.2. C/N ratio

Similar to C_{org}, nitrogen content accumulates very fast at the beginning of soil development in the topsoil at forest and grassland sites and levels off afterwards (see Appendix). Cropland sites have lower nitrogen contents, which increase slowly along the age gradient. Nitrogen content is decreasing in the subsoil.

The relationship of carbon to nitrogen is an important and common used factor giving information about carbon stabilisation and sequestration processes. The ratio also gives information of the ability of organic material to improve soil structure (Blanco-Canqui and Lal, 2004). High ratios indicate that organic material resists long times and improves soil aggregation and low C/N ratios enhance mineralization and a rapid decomposition (Blanco-Canqui and Lal, 2004).

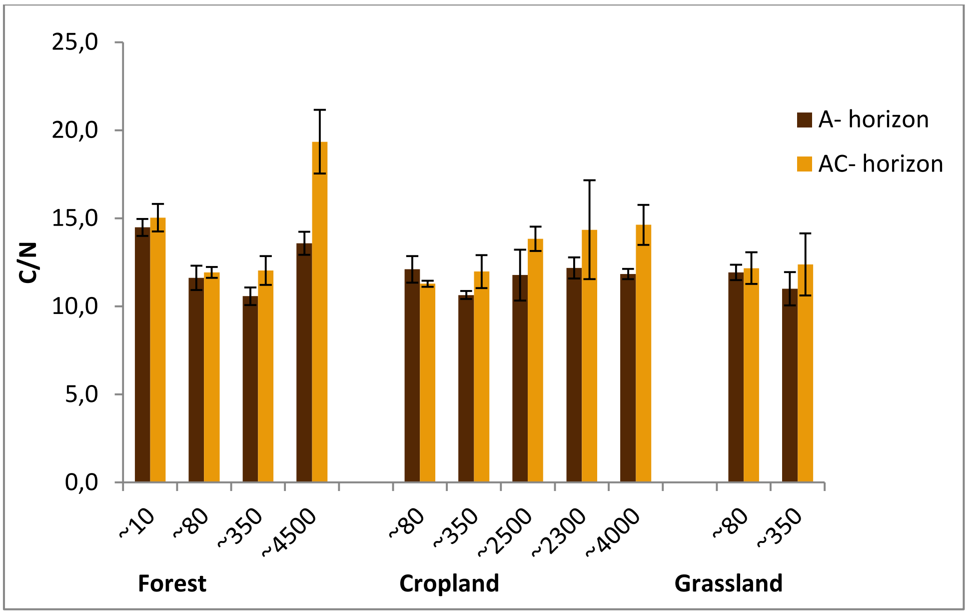


Figure 18: C/N ratio in the A and AC horizon

The C/N ratios range from 10.4 to 20.9 and there is no clear trend detectable along the chronosequence (see Figure 18). The values are in the middle range and indicate that decomposition in this small fraction may take an active role.

However, similar values between most sites would point to more similar composition of the SOM in the clay sized aggregates independent to their age and land use. The AC horizon has a higher ratio than the topsoil with time maybe due to their older or less decomposable SOM. In bulk soils the C/N ratio is usually decreasing in the AC horizon due to the lower SOM content and high nitrogen content (Rumpel and Kögel- Knabner, 2011). Some authors however found an increase of the C/N ratio in subsoil and explained the increase due to the presence of charred material (Rumpel and Kögel- Knabner, 2011).

4.3. Development of the A horizon in the Marchfeld

The carbon accumulation rate in the microstructure (< 2µm) is very fast during the early stage of soil development (see Figure 19) which is contributing to the formation of the A and AC horizons in the Fluvisols and Chernozems.

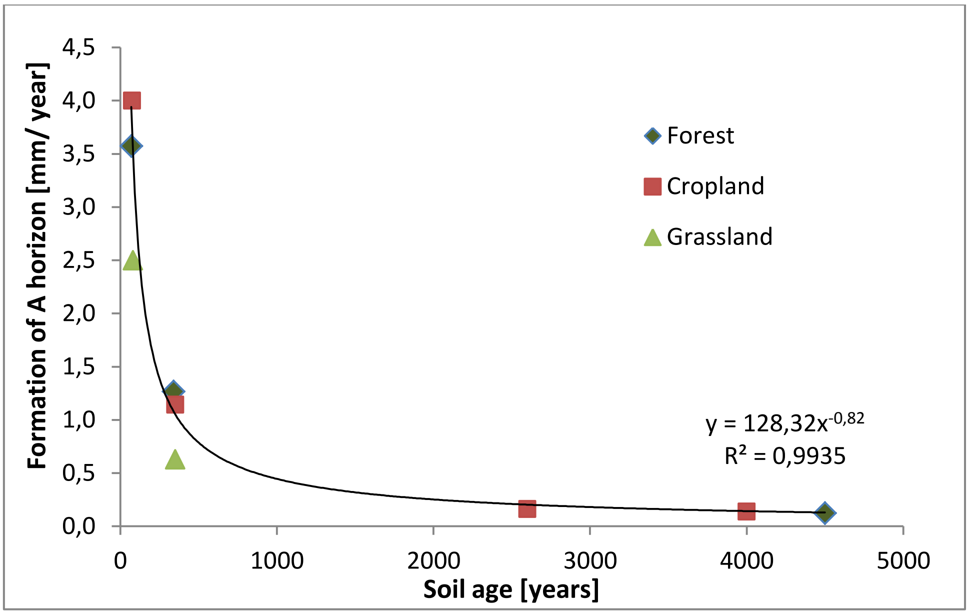


Figure 19: Soil formation rate in the Marchfeld

According to the depth of the AC horizons, soil development is fast at the beginning and slows down after ~350 years. At the beginning of soil formation the profile increases up to 4 mm per year. After 350 years the soil formation rate is however decreasing to 1.3- 0.5 mm per year. Old soils (> 2000 years) have a soil formation rate less than 0.1 mm new soil per year. "New soil" refers to the built up of microstructure (< 2 µm) containing a C_{org} concentration of more than one percent (compare with Figure 17).

4.4. Characterisation of soil organic matter pools in the clay sized aggregates

4.4.1. Simultaneous Thermal Analysis

The temperature limits for thermally labile and thermally resistant regions are not rigorously defined (Plante et al., 2009). Until 190°C usually an endothermic water release occurs (Plante et al., 2011). This region is therefore not considered in the analysis but was considered by calculating the SOM contents and the proportions of the different SOM pools. SOM oxidation is represented by the exothermic region between 190- 600°C (Plante et al., 2011). This exothermic region can be separated into three pools according to the thermal stability of soil organic matter (De la Rosa et al., 2008). As an example, a result of a STA is presented in Figure 20. It shows the big difference of the thermograms of the youngest forest site (orange curve) compared to the oldest (green curve).

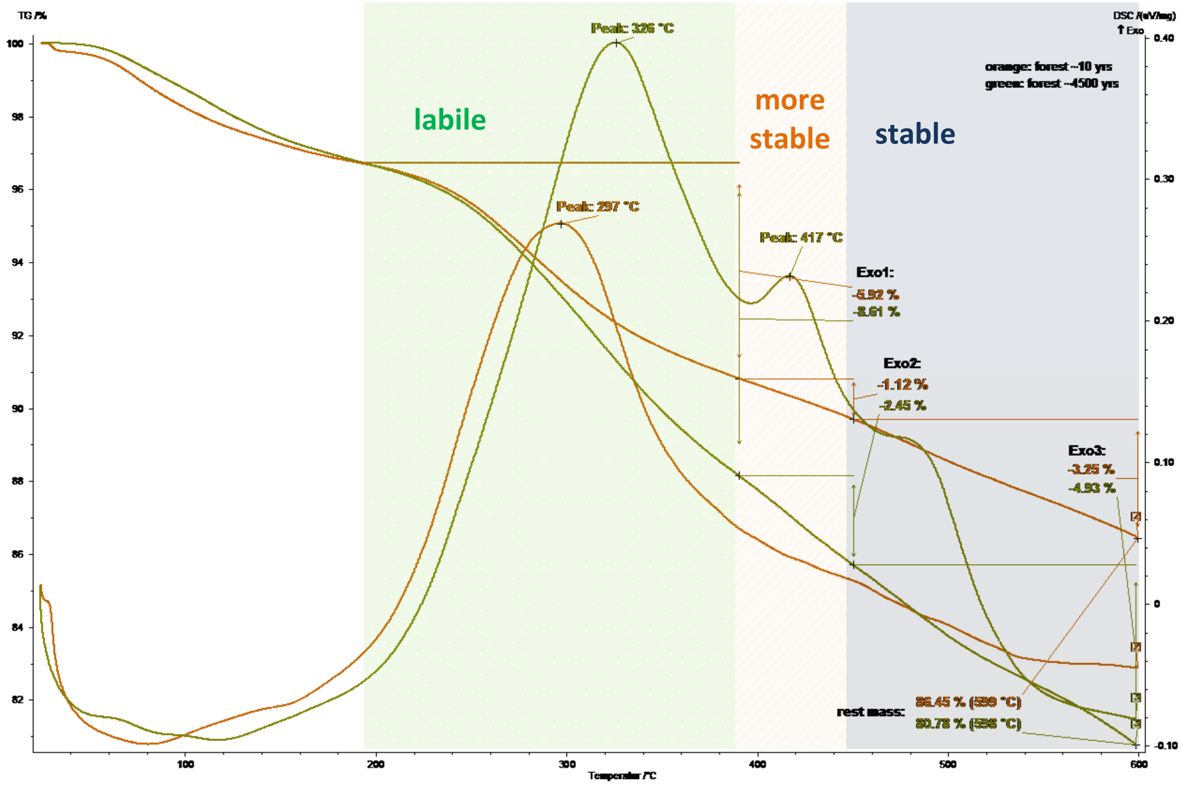


Figure 20: Output graph of the STA which shows the different curves of young versus old forest sites

More exothermic reactions can be noticed in the older soil

The weight loss and temperature limits in this study were slightly modified after the concept of Lopez- Capel et al. (2006) and De la Rosa et al. (2008) and were related to following pools:

- Exo1= labile pool: 190- 390°C
- Exo2= more stable pool: 390- 450°C
- Exo3= stable pool: 450- 600°C

The different pools were calculated as relative proportion of the total weight loss (Exo_{tot}) between 190 and 600°C (De la Rosa et al., 2008).

The mass loss of the labile pool Exo1 represents the oxidation of carbohydrates, proteins, cellulose and carboxyl groups (De la Rosa et al., 2008). Exo2 is attributed to polypehnolic and other aromatic structures like lignin (Lopez Capel et al., 2005; Rovira et al., 2008). Exo3 is the most stable fraction containing polycondensed aromatic black carbon (Del la Rosa et al., 2008).

Chapter 2.5. mentions that clay minerals do not affect exothermic reactions between 200- 600°C measured with the STA and a reason for choosing this method was its unproblematic use with soils containing carbonates as these start to decompose at temperatures above 600°C. Plante et al. (2011) concluded the influence of minerals by correlating the thermogravimetric mass losses in the exothermic region between 190- 600°C with sample organic carbon concentrations measured by elemental analysis. The ratio between TG mass loss and carbon was 2.06 which is higher than the "van Bemmelen factor" but new studies suggest a conversion factor of 2 (Plante et al., 2011). The ratio between the thermogravimetric mass loss and carbon in this study is around 2 at the beginning of soil formation and increases along the chronosequence in the AC horizon up to 4.4. The ratio in the A horizon stays almost constant. A possible explanation for this increase is that carbonates in this study do affect the exothermic reaction probably in the highest temperature region. The extremely high and increasing carbonate content along the soil age in the AC horizon could have affect the STA measurement and might explain the higher mass loss in the SOM decomposition region. Therefore the soil organic carbon content was converted with the factor of 2 to the soil organic matter content. Also Halloysite and Kaolinte show endothermic reactions between 500- 600°C (Plante et al., 2011) but the analysed soils do not contain halloysite and only a little amount of kaolinte.

4.4.2. Soil organic matter pools

Figure 21 represents the absolute amount of the different STA pools in the clay sized microaggregates.

As already mentioned above (see chapter 2.4.), some authors suggest that the clay- sized fraction mainly consists of the intermediate and passive (more stable) soil organic matter pool (von Lützow et al., 2007). Other studies with thermal analysis also showed that labile carbon is more bound to coarse fractions, the finer particle size fractions contain mainly refractory (more stable) material (Lopez- Capel et al., 2005).

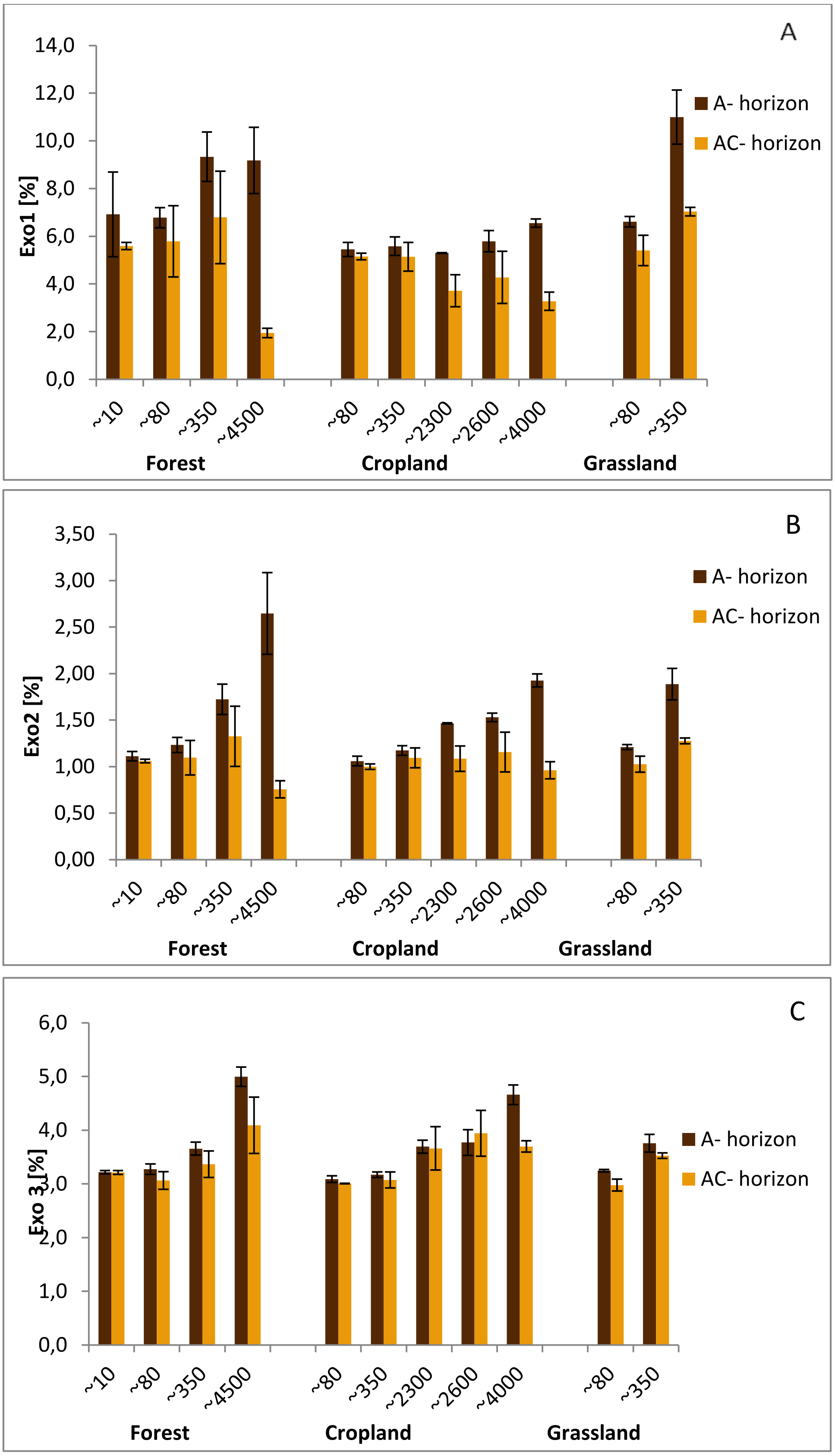


Figure 21: Distribution of different SOM pools in the clay sized microaggregates

A: Exo1= labile pool, 190- 390°C; B: Exo2= more stable pool, 390- 450°C;

C: Exo3= stable pool, 450- 600°C

The results presented here show that the labile pool also plays a big role in our clay sized aggregates and that the composition of SOM in the clay-sized fraction is influenced by land use.

Exo1 shows a strong increase from 80 to 350 years in the topsoil of the forest and grassland sites. The labile pool is almost constant in topsoils of cropland sites along the age gradient but contains a much lower content compared to all other soils. Plante et al. (2011) reported that labile SOM pools with rapid turnover times respond more rapidly to changes in environmental conditions. Stable SOM pools with low quality are usually left behind by microbes because they prefer to consume (mineralise) high quality (labile) soil organic matter (Plante et al., 2011).

Trends of the proportional composition of SOM are a bit different compared to the content of the different pools in the clay sized microaggregates (see Figure 22).

SOM at cropland sites contains less labile compounds than other land uses. The more stable and stable compounds are therefore the highest at cropland sites and show an increase along the age gradient. As already mentioned above, Exo3 mainly consists of black carbon which is a complex, polyaromatic substance produced under burning processes (Almendros et al., 2003). Up to the Second World War it was usual to burn leftovers of crop directly on the field which can explain the high proportion of Exo3. Also, fires in the forest or on grassland have been more usual than nowadays. This can explain the increase of Exo3 at soils older than 80 years.

Grassland and forest sites show an increase of labile components from 80 to 350 years which goes hand in hand with the rapid C_{org} accumulation at these sites (compare to Figure 17).

Microaggregates do not show a fast changing composition of SOM at the beginning of soil development. Shifts in the different pools are constant along the age gradient.

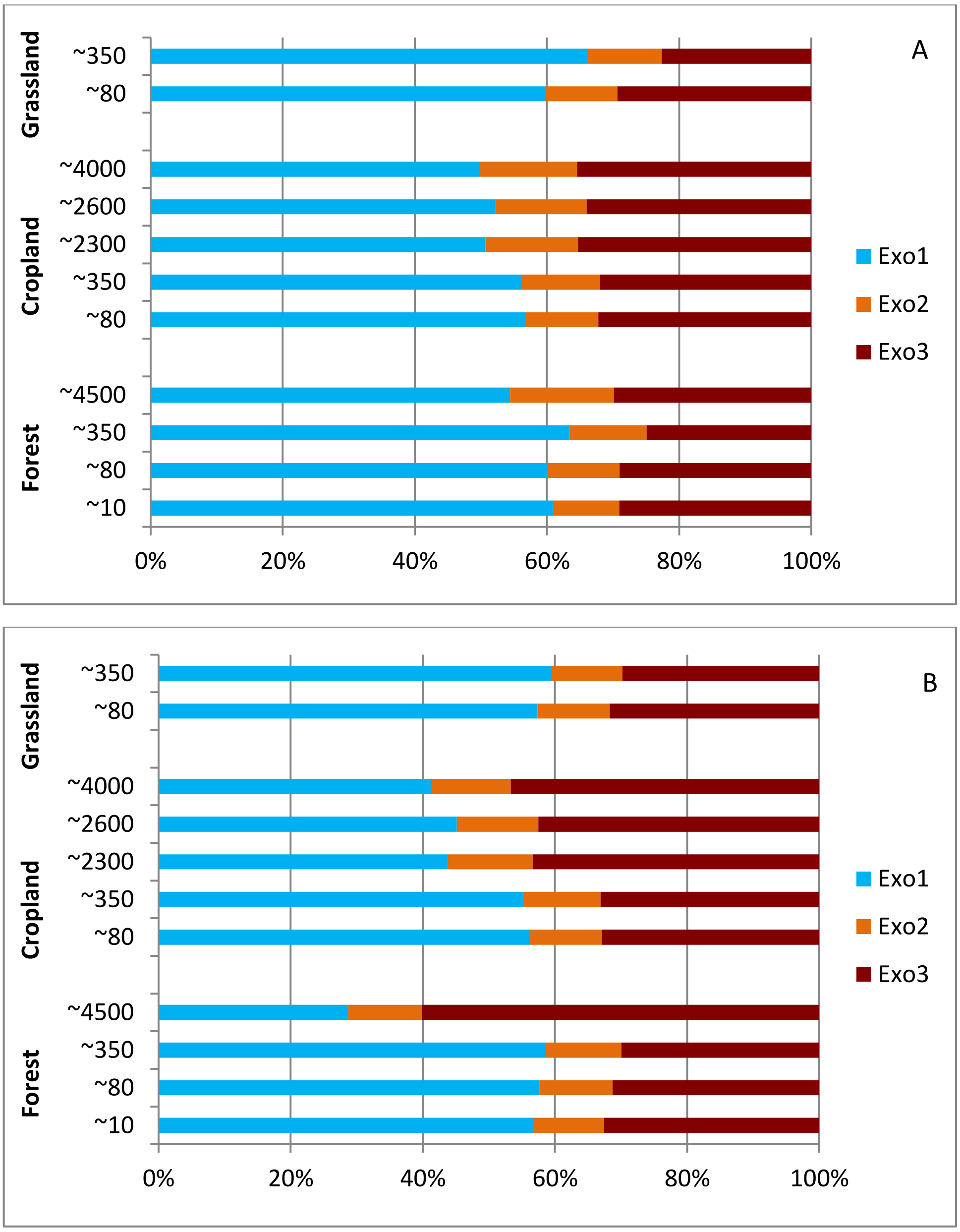


Figure 22: SOM composition (Exo1- Exo3) in the A and AC horizon according to labile (blue), more stable (orange) and stable (dark red) compounds
A: A horizon; B: AC horizon

Proportionally, the stable compounds (Exo 3) in the AC horizons (see Figure 22) are higher in all soils than in the corresponding A horizon. The stable SOM components in the AC horizon are increasing along the chronosequence. This affirmed one of the hypotheses that SOM in the AC horizon contains more stable compounds but as already mentioned above, a more detailed study needs to be performed on the subsoil.

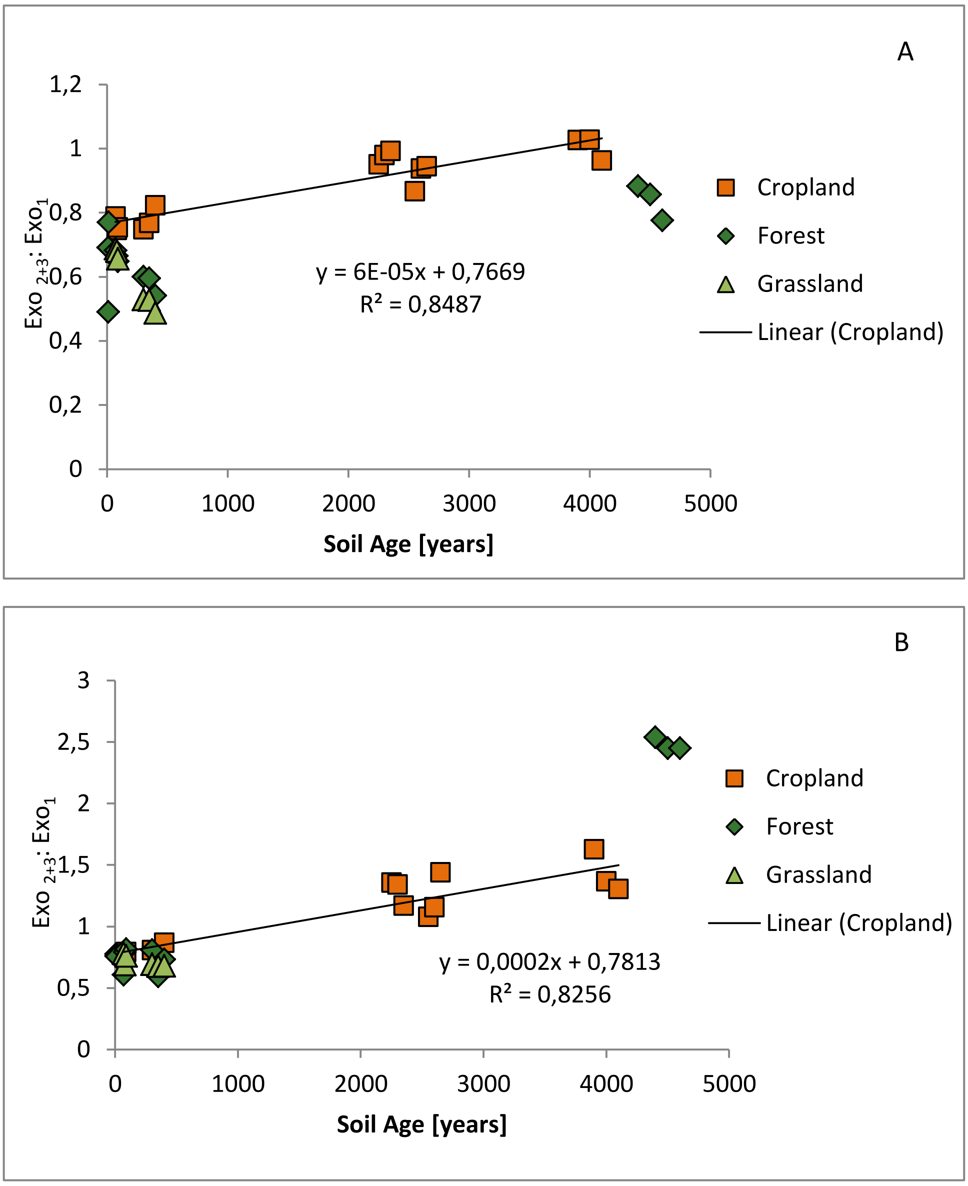


Figure 23: Ratio of Exo2+3:Exo1

An increase of the ratio indicates an increase of the stable pool compared to the labile

A: A horizon; B: AC horizon

In recent years studies successfully tested indices to allow a quantitative interpretation of thermal stability of organic matter (Plante et al., 2009). Lopez Capel et al. (2006) introduced the ratio Exo1/Exo2+3. This relationship gives information of how much labile SOM material, compared to the (more) stable material is in the soil. An increase of the relationship indicates that the content of the labile material decreases and the soil contains more of stable SOM.

In our clay sized aggregates this research an increase of the ratio Exo2+3/ Exo1 shows that the relative contribution of chemically stable to labile compounds is increasing. All ratios higher than 1 indicate that more stable than labile material is stored. Figure 23 represents the above conclusions that the ratio in the AC horizon is higher than in the A horizon. With time the ratio in the cropland sites is increasing in both horizons almost linear. The figure also shows that in the A horizon the SOM pool in the cropland sites is the most stable one. The oldest forest site in the AC horizon shows the highest amount of stable SOM.

4.4.3. Thermal peaks

Beside weight losses, endothermic and exothermic peaks can be observed. Usually two exothermic peaks in the temperature between 200- 500°C can be detected due to decomposition and combustion reaction of organic fractions with different thermal stabilites (Plante et al., 2009). The peak centred near 100°C represents endothermic reaction associated with hygroscopic water release (Kleber et al., 2011) and does not influence the characterization of SOM.

The exothermic peaks around 300°- 350°C (see Figure 20) can be related to decomposition of labile material (cellulose, decarboxylation) and the peak around 450°C can be attributed to recalcitrant and/or char material (De la Rosa et al., 2008).

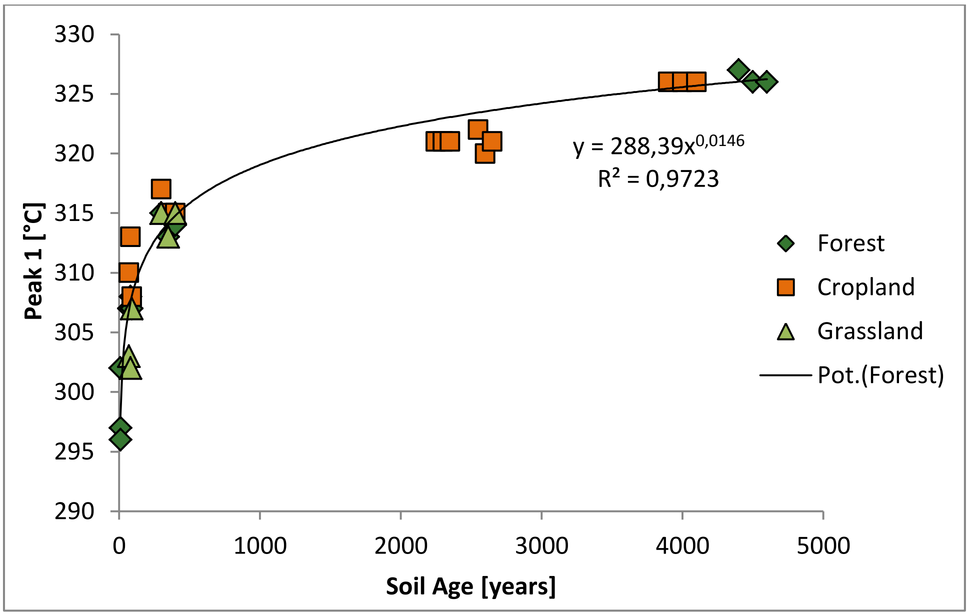


Figure 24: Peak at ~ 300 °C in the A horizon

All samples have their main exothermic peak at ~300°C. The temperature level of this peak increases potential with increasing soil age (see Figure 24). Cropland sites have a higher peak compared to the other land uses in the same age group. This would be an indicator describing that labile organic matter is more “stable” in cropland sites because higher temperature is needed to burn the material. The AC horizon behaves similar to the A horizon.

The second peak around 450°C only appears in the soil samples older than 2000 years and does not show a trend in soils of different age or in soils of different land use management. The data is however not good comparable due to the small amount of results in this case.
There can be a third exothermic peak at 550-650° where material like black carbon and/or kerogen are combusted (De la Rosa et al., 2008). None of the measured clay sized aggregate fractions show such a third peak. The old soils however show a shoulder at this temperature level (compare Figure 20).

5. CONCLUSIONS

The analysed soils in this research developed on the same parent material but differ in their soil age and land use. All measured soil properties showed a distinct time trend but also an influence of land use management. Therefore, soil age should receive more attention analysing physical and chemical soil properties when dealing with sensitive topics like carbon accumulation.

Organic carbon content on clay sized aggregates (<2 µm) accumulation is increasing along the age gradient in the topsoil. Its content and accumulation rate was lower in cropland. The C_{org} content at forest sites increases very fast in the first 350 years and levels off afterwards.

It is assumed that this is caused by the saturation of clay sized particles after the first decades of soil development. The cropland sites show a slow, but linear increase of C_{org} content with time. There the system is continuously disrupted and so no equilibrium is reached. This shows that land use management has a stronger effect on SOM content than decades of soil formation.

Splitting up the SOM content in different SOM pools, cropland shows the lowest amount of labile and the highest amount of stable components. This difference is increasing along the age gradient although grassland and forest site also shows a more stable composition with soil age.

All AC horizons show a lower C_{org} content than the corresponding topsoil but they contain and accumulate stable organic material to a higher rate. The decreasing C_{org} content in soils with higher age indicates that the C_{org} content is dependent on the depth of the AC horizon.

6. OUTLOOK

To make clear statements and to analyse the mechanisms and reasons behind the received data, more research is needed. Further analysis of Fe and Al oxides along the age gradient promises to give information for a better understanding of SOM accumulation processes. Beside Fe and Al oxides, the mineralogy and surface charge characteristics give clay minerals the capacity to adsorb OM (Baldock and Skjemstad, 2000). Studies showed that C is not just a function of clay content but has to be correlated with the specific surface are (Baldock and Skjemstad, 2000). At the current research state, processes in the subsoil are not completely clear. The subsoil is a very complex system. Soils in the presented study are strongly influenced by changing groundwater tables during the last centuries. Analysis of complete soil profiles as well as the installation of suction cups in some soil profiles allow insights into transport processes into subsoil.

The STA is a good method to get a rough inside in the composition of soil organic matter but might be influenced by carbonates in our soil as the ratio of SOM content (Exo1-3) to C_{org} is above 2 in the AC horizon. A ^{13}C CPNMR analysis can give more a detailed information about the chemical components of soil organic matter stored in the samples and could help for a better explanation of the presented data.

Chapter 2.3.3. mentions that Kleber et al. (2011) assume that microbial ecology mainly influences the organic matter turnover. The microbiological factor has so far not been considered to a high extend. After receiving more information (^{13}C CPNMR) it might be necessary to compare the SOM composition data with the content and activity of microbial organisms.

All measurements are carried out on clay sized microaggregates. For a whole picture it is however necessary to compare the data with measurements on the bulk soil or other aggregate classes.

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8. APPENDIX

Sam-ple	Depth	Land use	Soil age [yrs]	pH (H_2O)	Clay Content [%]	Carbo-nates [%]	EW aggrega-tes [%]	SOM content [g kg^{-1}]	C_{tot} content [[%]	N_{tot} content [%]	C_{org} content [%]	C/N
1C$_1$	0-10	forest	9	7.52	11.7	16.7	8.8	85.8	6.29	0.29	4.29	14.75
1C$_2$	0-10	forest	10	7.66	7.4	20.1	4.6	78.6	6.34	0.28	3.93	13.92
1C$_3$	0-10	forest	11	7.55	10.2	18.6	2.8	79.9	6.23	0.27	3.99	14.77
2A$_1$	0-10	grassland	70	7.65	14.4	17.4	18.7	80.8	6.13	0.33	4.04	12.22
2A$_2$	0-10	grassland	80	7.57	9.8	15.6	7.8	86.7	6.21	0.36	4.33	12.13
2A$_3$	0-10	grassland	90	7.63	12.5	16.8	14.1	95.7	6.80	0.42	4.78	11.42
2B$_1$	0-10	cropland	70	7.82	16.2	22.4	3.6	64.1	5.89	0.27	3.20	11.86
2B$_2$	0-10	cropland	80	7.92	14.1	21.7	0.0	71.0	6.16	0.31	3.55	11.50
2B$_3$	0-10	cropland	90	7.84	13.1	19.6	0.0	78.5	6.27	0.30	3.92	12.94
2C$_1$	0-10	forest	70	7.59	15.2	20.7	12.5	100.0	7.49	0.45	5.00	11.03
2C$_2$	0-10	forest	80	7.59	10.5	18.6	9.1	94.0	6.93	0.38	4.70	12.37
2C$_3$	0-10	forest	90	7.57	12.1	19.2	13.5	104.3	7.52	0.46	5.22	11.45
3A$_1$	0-10	grassland	300	7.61	15.0	12.4	21.4	135.2	8.25	0.65	6.76	10.42
3A$_2$	0-10	grassland	350	7.51	13.9	13.4	17.5	141.2	8.66	0.58	7.06	12.09
3A$_3$	0-10	grassland	400	7.40	11.4	11.0	19.6	175.2	10.08	0.83	8.76	10.50
3B$_1$	0-10	cropland	300	7.90	22.3	13.1	2.0	74.4	5.29	0.36	3.72	10.40
3B$_2$	0-10	cropland	350	7.97	18.8	11.6	4.1	76.6	5.22	0.35	3.83	10.85
3B$_3$	0-10	cropland	400	7.94	24.4	13.5	5.7	66.8	4.96	0.31	3.34	10.67
3C$_1$	0-10	forest	300	7.63	17.4	13.3	15.4	107.0	6.95	0.54	5.35	10.00
3C$_2$	0-10	forest	350	7.68	16.5	9.6	11.2	123.8	7.35	0.57	6.19	10.85
3C$_3$	0-10	forest	400	7.54	15.3	9.8	9.4	154.0	8.87	0.71	7.70	10.88
4B$_1$	0-10	cropland	2550	8.04	17.1	11.1	0.0	81.2	5.40	0.40	4.06	10.19
4B$_2$	0-10	cropland	2600	7.84	18.2	9.8	0.0	73.0	4.83	0.30	3.65	12.12
4B$_3$	0-10	cropland	2650	8.00	15.4	13.8	0.0	85.2	5.92	0.33	4.26	13.03
5B$_1$	0-10	cropland	2250	8.27	19.3	11.5	2.0	68.0	4.78	0.27	3.40	12.43
5B$_2$	0-10	cropland	2300	8.34	19.3	9.9	2.1	78.4	5.11	0.31	3.92	12.62
5B$_3$	0-10	cropland	2350	8.40	18.1	12.1	2.4	79.6	5.43	0.35	3.98	11.49
6B$_1$	0-10	cropland	3900	8.07	19.9	21.7	0.0	92.5	7.24	0.39	4.63	11.77
6B$_2$	0-10	cropland	4000	8.07	20.8	19.2	0.0	97.3	7.17	0.40	4.87	12.16
6B$_3$	0-10	cropland	4100	8.04	21.3	16.3	0.0	103.9	7.16	0.45	5.20	11.58
6C$_1$	0-10	forest	4400	7.90	17.8	25.1	8.2	134.0	9.71	0.49	6.70	13.78
6C$_2$	0-10	forest	4500	7.89	18.7	21.5	7.5	149.1	10.03	0.53	7.46	14.10
6C$_3$	0-10	forest	4600	7.87	20.9	12.6	9.5	190.9	11.06	0.74	9.54	12.86
1C$_1$	40-45	forest	9	7.92	6.7	15.3	0.0	74.8	5.57	0.26	3.74	14.64
1C$_2$	40-45	forest	10	7.92	7.2	16.0	1.6	73.3	5.59	0.23	3.66	15.94
1C$_3$	40-45	forest	11	7.95	7.0	16.6	0.0	71.7	5.58	0.25	3.58	14.53
2A$_1$	25-35	grassland	70	7.75	15.3	22.9	18.2	73.4	6.42	0.28	3.67	12.92
2A$_2$	25-35	grassland	80	7.63	13.3	18.9	11.8	81.6	6.35	0.33	4.08	12.42
2A$_3$	25-35	grassland	90	7.61	12.8	22.6	15.3	67.8	6.11	0.30	3.39	11.17

$2B_1$	25-35	cropland	70	7.87	16.7	22.5	0.0	72.5	6.32	0.32	3.62	11.46
$2B_2$	25-35	cropland	80	7.94	17.1	21.9	0.0	65.8	5.92	0.29	3.29	11.28
$2B_3$	25-35	cropland	90	8.04	15.2	21.8	0.0	62.4	5.74	0.28	3.12	11.12
$2C_1$	20-30	forest	70	7.81	16.4	21.8	8.5	88.6	7.05	0.37	4.43	11.91
$2C_2$	20-30	forest	80	7.87	17.3	24.5	2.3	59.4	5.90	0.26	2.97	11.63
$2C_3$	20-30	forest	90	8.08	15.0	21.7	0.0	59.5	5.57	0.24	2.97	12.25
$3A_1$	15-30	grassland	300	7.96	16.1	20.8	28.9	81.3	6.56	0.28	4.07	14.41
$3A_2$	15-30	grassland	350	7.89	13.6	14.7	14.5	90.7	6.30	0.40	4.54	11.27
$3A_3$	15-30	grassland	400	8.00	12.0	18.0	13.5	90.4	6.68	0.39	4.52	11.47
$3B_1$	35-45	cropland	300	8.01	22.3	15.1	0.0	74.2	5.52	0.33	3.71	11.29
$3B_2$	35-45	cropland	350	8.21	13.7	14.8	0.0	62.6	4.91	0.27	3.13	11.59
$3B_3$	35-45	cropland	400	8.00	23.1	12.8	0.0	70.0	5.04	0.27	3.50	13.05
$3C_1$	35-45	forest	300	8.02	19.4	15.0	11.5	71.5	5.37	0.30	3.57	12.05
$3C_2$	35-45	forest	350	8.17	17.0	13.3	2.4	71.4	5.16	0.28	3.57	12.85
$3C_3$	35-45	forest	400	7.91	14.7	15.3	9.5	74.1	5.54	0.33	3.71	11.22
$4B_1$	40-45	cropland	2550	8.35	12.2	21.6	0.0	63.4	5.77	0.23	3.17	13.84
$4B_2$	40-45	cropland	2600	8.40	19.0	26.2	0.0	63.8	6.33	0.24	3.19	13.15
$4B_3$	40-45	cropland	2650	8.47	12.9	37.9	0.0	43.7	6.73	0.15	2.19	14.52
$5B_1$	75-90	cropland	2250	8.51	31.2	34.0	4.5	44.8	6.32	0.13	2.24	17.55
$5B_2$	75-90	cropland	2300	8.39	18.9	23.8	4.2	54.2	5.56	0.21	2.71	13.15
$5B_3$	75-90	cropland	2350	8.49	20.8	27.1	0.0	56.9	6.10	0.23	2.84	12.36
$6B_1$	50-60	cropland	3900	8.55	11.8	51.1	0.0	38.7	8.07	0.13	1.93	14.88
$6B_2$	50-60	cropland	4000	8.44	16.3	56.5	0.0	43.8	8.97	0.14	2.19	15.61
$6B_3$	50-60	cropland	4100	8.43	16.1	52.8	0.0	47.5	8.71	0.18	2.38	13.39
$6C_1$	50-60	forest	4400	8.67	14.5	56.8	8.2	31.8	8.41	0.09	1.59	17.40
$6C_2$	50-60	forest	4500	8.68	16.2	58.7	8.6	30.8	8.58	0.08	1.54	19.67
$6C_3$	50-60	forest	4600	8.63	6.5	68.9	8.0	26.8	9.60	0.06	1.34	20.97

Sam-ple	Depth	Land use	Soil age [yrs]	Exo1 SOM [g kg-1]	Exo2 SOM [g kg-1]	Exo3 SOM [g kg-1]	Exo 1 total [%]	Exo2 total [%]	Exo3 total [%]	Exo2+3/ Exo1	Peak 2 [°C]	Peak3 [°C]
$1C_1$	0-10	forest	9	591.2	108.5	300.3	6.3	1.2	3.2	0.69	302	
$1C_2$	0-10	forest	10	671.2	84.3	244.5	8.9	1.1	3.3	0.49	297	
$1C_3$	0-10	forest	11	565.0	108.5	326.5	5.5	1.1	3.2	0.77	296	
$2A_1$	0-10	grassland	70	592.3	109.7	298.0	6.5	1.2	3.3	0.69	303	
$2A_2$	0-10	grassland	80	595.0	109.3	295.7	6.5	1.2	3.2	0.68	302	
$2A_3$	0-10	grassland	90	603.9	109.2	287.0	6.9	1.2	3.3	0.66	307	
$2B_1$	0-10	cropland	70	559.2	109.6	331.1	5.1	1.0	3.0	0.79	310	
$2B_2$	0-10	cropland	80	572.9	110.1	317.0	5.6	1.1	3.1	0.75	313	
$2B_3$	0-10	cropland	90	570.0	111.6	318.5	5.6	1.1	3.1	0.75	308	
$2C_1$	0-10	forest	70	594.3	107.5	298.1	6.3	1.1	3.2	0.68	307	
$2C_2$	0-10	forest	80	600.5	111.3	288.2	7.0	1.3	3.3	0.67	308	
$2C_3$	0-10	forest	90	606.7	108.8	284.5	7.1	1.3	3.3	0.65	307	
$3A_1$	0-10	grassland	300	653.8	112.3	233.8	10.0	1.7	3.6	0.53	315	
$3A_2$	0-10	grassland	350	654.9	114.4	230.7	10.8	1.9	3.8	0.53	313	
$3A_3$	0-10	grassland	400	672.5	113.2	214.3	12.2	2.1	3.9	0.49	315	
$3B_1$	0-10	cropland	300	572.0	118.0	310.0	6.0	1.2	3.2	0.75	317	
$3B_2$	0-10	cropland	350	565.7	117.2	317.2	5.6	1.2	3.1	0.77	315	
$3B_3$	0-10	cropland	400	548.6	119.5	331.9	5.2	1.1	3.1	0.82	315	
$3C_1$	0-10	forest	300	624.9	115.8	259.3	8.5	1.6	3.5	0.60	315	
$3C_2$	0-10	forest	350	626.8	118.1	255.1	9.0	1.7	3.7	0.60	313	
$3C_3$	0-10	forest	400	648.9	117.4	233.6	10.5	1.9	3.8	0.54	314	
$4B_1$	0-10	cropland	2550	535.7	135.9	328.5	6.2	1.6	3.8	0.87	322	418
$4B_2$	0-10	cropland	2600	516.0	144.2	339.8	5.3	1.5	3.5	0.94	320	411
$4B_3$	0-10	cropland	2650	514.1	134.3	351.6	5.8	1.5	4.0	0.95	321	411
$5B_1$	0-10	cropland	2250	512.6	141.7	345.6	5.3	1.5	3.6	0.95	321	418
$5B_2$	0-10	cropland	2300	505.2	140.1	354.6	5.3	1.5	3.7	0.98	321	411
$5B_3$	0-10	cropland	2350	501.9	138.9	359.2	5.3	1.5	3.8	0.99	321	412
$6B_1$	0-10	cropland	3900	493.4	144.1	362.5	6.4	1.9	4.7	1.03	326	410
$6B_2$	0-10	cropland	4000	493.2	144.1	362.6	6.6	1.9	4.8	1.03	326	409
$6B_3$	0-10	cropland	4100	509.5	151.6	338.9	6.7	2.0	4.5	0.96	326	411
$6C_1$	0-10	forest	4400	531.3	153.0	315.8	8.2	2.4	4.9	0.88	327	416
$6C_2$	0-10	forest	4500	538.5	152.6	308.9	8.6	2.4	4.9	0.86	326	417
$6C_3$	0-10	forest	4600	563.1	164.8	272.1	10.8	3.2	5.2	0.78	326	421
$1C_1$	40-45	forest	9	562.7	107.8	329.5	5.4	1.0	3.2	0.78	298	
$1C_2$	40-45	forest	10	568.0	107.5	324.5	5.6	1.1	3.2	0.76	299	
$1C_3$	40-45	forest	11	569.6	107.4	323.1	5.7	1.1	3.3	0.76	300	
$2A_1$	25-35	grassland	70	561.1	108.6	330.3	4.9	1.0	2.9	0.78	313	
$2A_2$	25-35	grassland	80	591.9	108.3	299.8	6.1	1.1	3.1	0.69	314	
$2A_3$	25-35	grassland	90	567.8	110.5	321.7	5.2	1.0	2.9	0.76	316	
$2B_1$	25-35	cropland	70	566.5	110.5	323.0	5.3	1.0	3.0	0.77	310	
$2B_2$	25-35	cropland	80	562.7	109.1	328.2	5.2	1.0	3.0	0.78	314	
$2B_3$	25-35	cropland	90	557.9	108.0	334.1	5.0	1.0	3.0	0.79	313	
$2C_1$	20-30	forest	70	622.2	108.5	269.3	7.5	1.3	3.3	0.61	310	
$2C_2$	20-30	forest	80	557.8	110.0	332.2	4.9	1.0	2.9	0.79	309	
$2C_3$	20-30	forest	90	550.8	112.8	336.3	4.9	1.0	3.0	0.82	314	

$3A_1$	15-30	grassland	300	590.8	108.1	301.0	6.8	1.3	3.5	0.69	315	
$3A_2$	15-30	grassland	350	596.5	109.4	294.1	7.1	1.3	3.5	0.68	316	
$3A_3$	15-30	grassland	400	595.2	106.0	298.8	7.1	1.3	3.6	0.68	315	
$3B_1$	35-45	cropland	300	553.6	118.6	327.8	5.4	1.2	3.2	0.81	315	
$3B_2$	35-45	cropland	350	565.7	117.2	317.2	5.6	1.2	3.1	0.77	315	
$3B_3$	35-45	cropland	400	535.4	116.4	348.1	4.5	1.0	2.9	0.87	314	
$3C_1$	35-45	forest	300	553.0	112.3	334.7	5.3	1.1	3.2	0.81	314.0	
$3C_2$	35-45	forest	350	626.8	118.1	255.1	9.0	1.7	3.7	0.60	313.0	
$3C_3$	35-45	forest	400	577.8	115.0	307.3	6.1	1.2	3.3	0.73	313.0	
$4B_1$	40-45	cropland	2550	481.1	122.9	396.0	5.1	1.3	4.2	1.08	323	417
$4B_2$	40-45	cropland	2600	463.6	124.0	412.4	4.7	1.3	4.2	1.16	323	412
$4B_3$	40-45	cropland	2650	410.0	123.1	466.8	3.0	0.9	3.5	1.44	322	413
$5B_1$	75-90	cropland	2250	424.2	129.3	446.5	3.1	0.9	3.2	1.36	326	416
$5B_2$	75-90	cropland	2300	427.3	136.3	436.5	3.7	1.2	3.8	1.34	322	414
$5B_3$	75-90	cropland	2350	461.2	120.5	418.2	4.4	1.2	4.0	1.17	320	411
$6B_1$	50-60	cropland	3900	380.6	123.4	496.1	2.9	0.9	3.8	1.63	325	410
$6B_2$	50-60	cropland	4000	422.3	114.0	463.7	3.3	0.9	3.6	1.37	325	405
$6B_3$	50-60	cropland	4100	433.8	125.3	440.9	3.7	1.1	3.7	1.31	326	406
$6C_1$	50-60	forest	4400	282.6	111.4	606.0	2.1	0.8	4.5	2.54	321	426
$6C_2$	50-60	forest	4500	289.9	111.1	599.0	1.8	0.7	3.7	2.45	319	424
$6C_3$	50-60	forest	4600	289.9	111.1	599.0	1.8	0.7	3.7	2.45	319	426