

**Sustainable management of organic matter in a Swiss
arable soil - carbon sequestration dynamics under various
farming systems**

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“Life makes soil. Soil makes more life. [...] Life and soil were partners until modern agriculture changed the game.”

- David R. Montgomery in 'Dirt: The Erosions of Civilizations'

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Summary

Soils, often overlooked and underestimated, are intricate ecosystems that support a diverse array of organisms, contribute to global biogeochemical cycles, and play a pivotal role in food production. In addition to being the largest reservoir of terrestrial carbon (C) and a vital regulator of the global climate, soils provide a multitude of ecological services that are essential for the functioning of natural environments and fundamental for human well-being. The ability of arable soils to act as long-term C sinks through the process of C sequestration, directly influences the extent to which human-induced increases in atmospheric carbon dioxide (CO₂) can be offset and thus the extent to which climate change can be mitigated. However, the intensive and unsustainable use of arable soils has led to significant losses of soil organic matter (SOM), the storage medium of C in soil, which was accompanied by the loss of soil fertility. This prompted efforts to restore and increase SOM contents in soils through sustainable management, including economically incentivized C farming practices. The **overall objective** of this thesis was to improve our understanding of how various farming systems influence the dynamics of SOM within the soil. Particular emphasis was given to acquiring detailed insights into the mechanisms that govern SOM stability within different soil fractions. This would consequently allow the evaluation of different soil management strategies in terms of their effectiveness to contribute to climate change mitigation.

To achieve this objective, the **DOK long-term farming system comparison trial** in Switzerland served as an experimental platform for the observation of SOM dynamics. The focus was on four farming systems with different fertilizer types and quantities. A purely minerally fertilized system (CONMIN), a mixed-fertilized system receiving mineral and organic fertilizer as stacked farmyard manure (CONFYM) and a purely organically fertilized system receiving composted manure (BIODYN) were compared with an unfertilized control (NOFERT), over a period of 36 years (1982-2017).

In the **first study**, physical fractionation was used to separate functionally distinct SOM fractions from archived soil samples. The findings revealed that no additional soil organic carbon (SOC) was sequestered in the finest separated soil fraction (<6.3 μm) under any of the farming systems over the whole observation period. The focus on this specific fraction is driven by its significance for long-term C sequestration, as the association of SOM with fine minerals (referred to as MAOM, mineral-associated organic matter) ensures the highest level of stability. The increase of bulk SOC in BIODYN (+13%) and CONFYM (+5%) (CONMIN: -8%; NOFERT: -20%), indicates that additional C accumulation was only recorded in the form of highly labile particulate organic matter (POM), more specifically, occluded particulate organic matter (oPOM), which undergoes initial stabilization via incorporation into aggregates. Interestingly, BIODYN showed the highest oPOM-C, although OM inputs via organic

fertilizers were 20% lower compared to CONFYM. This indicates that the **qualitative differences of the organic manures are vital for C sequestration and thus for increasing soil fertility**. However, this labile fraction was prone to rapid losses within a few days. Considering that POM serves as a precursor to the highly stabilized MAOM, POM losses should be urgently avoided, as this impedes the potential for subsequent long-term C sequestration. Overall, these findings highlight the substantial dependence of soil fertility on the consistent application of organic fertilizers. Furthermore, in the context of climate change mitigation, it is very concerning that **even under sustainable management practices over several decades, additional long-term C sequestration was insufficient**. This finding was particularly surprising, especially considering that the saturation of the MAOM fraction could be ruled out as a contributing factor. In an effort to fully comprehend this observation, the second study was dedicated exclusively to the detailed examination of the MAOM fraction.

Consequently, the **second study** focused around the elucidation of the turnover dynamics within the MAOM fraction. MAOM samples from 1982 and 2017 were subjected to specific surface area (SSA) measurements before and after removal of OM with sodium hypochlorite (NaOCl). SSA results indicated **best conditions for MAOM-C stabilization under organic fertilization** and different sorption mechanisms in MAOM between farming systems with and without organic fertilization. In addition, ^{14}C radiocarbon analysis of the MAOM fraction and subsequent estimation of its mean residence times (MRT = measure for SOM permanence in the soil) were performed, using a model that takes into account 'bomb ^{14}C ' and radioactive decay. Based on the findings of the first study, which indicated unchanged MAOM-C contents in BIODYN and CONFYM, we expected that long-term organic fertilization would enhance MAOM stability, resulting in longer MRTs. However, the findings demonstrated that continuous organic fertilization led to substantially higher MAOM-C turnover rates and significantly shorter MRTs (BIODYN: 140 ± 19 yrs, CONFYM: 138 ± 18 yrs) in comparison to non-organic fertilization (CONMIN: 195 ± 27 yrs, NOFERT: 238 ± 40 yrs). This indicated that **MAOM is much more active under organic fertilization**. This apparent contradiction, where increased MAOM-C turnover appeared to contribute to constant MAOM-C contents, could however be explained with the concept of '**dynamic stability**'. A detailed visualization of this rather complex concept is given in **Figure 4.1** of this thesis.

The results of this thesis provide compelling evidence that the targeted efforts towards increased long-term C sequestration under agricultural management are insufficient. This dampens the high expectations for soil as a potent solution to bring about mitigated climate change. However, these findings fully align with the gradual and increasingly pronounced shift within the scientific community towards prioritizing soil management practices that promote soil fertility, rather than solely focusing on soil management for C sequestration as a means to address climate change. This thesis demonstrated that sustainable organic soil management, accompanied by consistent organic fertilizer inputs, emerges

as the most favorable approach in this regard. Specifically, in the case of BIODYN, despite solely increasing C contents in the labile SOM fractions, this can have a beneficial impact on climate, as long as this management approach is sustained.

List of abbreviations

^{14}C	radiocarbon
AMS	accelerator mass spectrometry
C	carbon
CO_2	carbon dioxide
CRP	crop rotation period
F^{14}C	Fraction Modern carbon
fPOM	free particulate organic matter
GHG	greenhouse gas
H_2O_2	hydrogen peroxide
HCl	hydrogen chloride
HF	hydrofluoric acid
LTE	long-term experiment
LU	livestock unit
LUC	land use change
MAOM	mineral-associated organic matter
MRT	mean residence time
N	nitrogen
Na	sodium
$\text{Na}_6\text{O}_{18}\text{P}_6$	sodium hexametaphosphate
NanoSIMS	nanoscale secondary ion mass spectrometry
NMR	nuclear magnetic resonance
OC	organic carbon
OM	organic matter
oPOM	occluded particulate organic matter
P	phosphorus
Pg	petagram
POM	particulate organic matter
ppm	parts per million
P-XRD	powder X-ray diffraction
RMSE	root-mean-square error
SOC	soil organic carbon
SOM	soil organic matter
SSA	specific surface area

CHAPTER 1:

GENERAL INTRODUCTION

1.1. Hot topic: Climate change and the role of soils in the global C cycle

Over the last six decades, the world's population has increased by an average of 80 million per year, from about 3.0 billion in 1960 to 7.9 billion in 2021, representing a total increase of 163% (UN, 2022). The increase in population came with a corresponding increase in food and energy demand, land consumption and degradation, subjecting agroecosystems to mounting pressures. Consequently, emissions of greenhouse gases (GHG), such as carbon dioxide (CO₂), the main anthropogenic contributor to climate change (Myrhe et al., 2013), have significantly increased during that period. As a result, atmospheric CO₂ concentrations continuously increased and reached a new temporary record high in 2021 (414.7 ppm), accompanied by increasing global temperatures (**Figure 1.2**) (Friedlingstein et al., 2022).

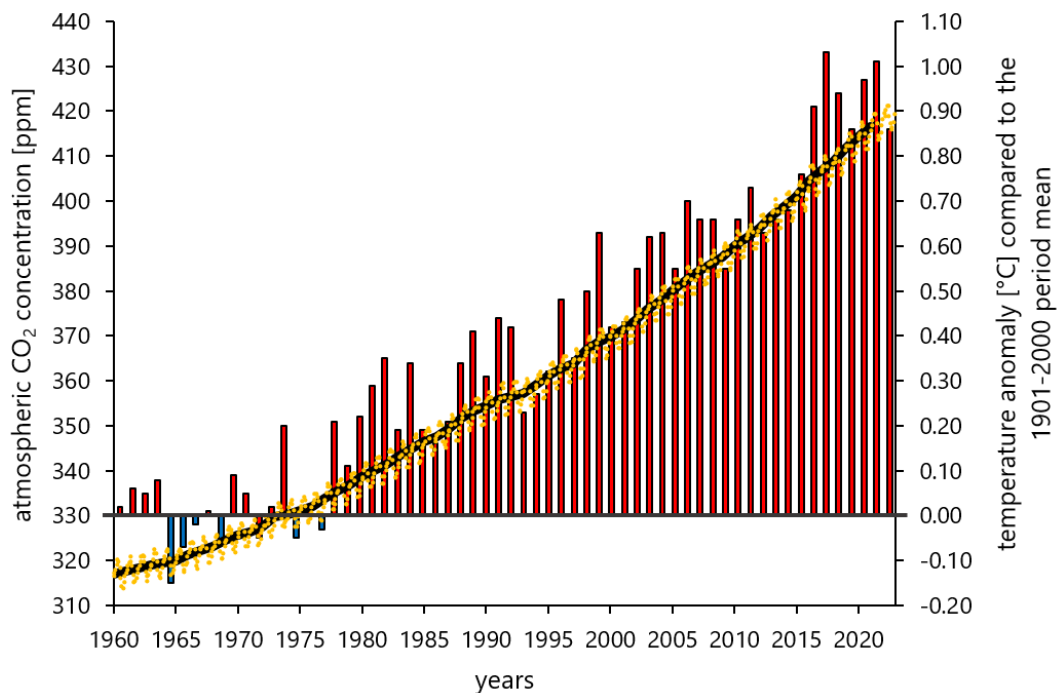


Figure 1.2: Development of global atmospheric CO₂ concentration and surface temperature anomalies from 1960 to 2021. Mean annual atmospheric CO₂ concentrations are given in parts per million [ppm] (black line), constructed from monthly mean values (yellow dots), recorded at Mauna Loa Observatory (Hawaii). Columns show surface temperature anomalies compared to the mean for the period 1901–2000. Blue columns indicate cooler-than-average and red columns warmer-than-average years. Own illustration, data originates from Tans and Keeling (2023).

According to estimates of the Food and Agriculture Organization of the United Nations (FAO), approximately 30% of the global population (2.3 billion people) experienced moderate or severe food insecurity in 2021, and about 760 million people even suffered from hunger (FAO et al., 2022). According to the United Nations (UN, 2022), the projected growth in global population to 9.7 billion by 2050 will lead to even greater demands for food and fuel (Fargione et al., 2008). Consequently, this surge in demand will further increase GHG emissions and intensify global warming (Chiari and Zecca, 2011; Peters

et al., 2012). Alarming, forecasts of record-breaking increases in global temperatures for the upcoming five years (UN, 2023), have raised concerns about the potential for "phenomenal human suffering" (Carrington, 2023).

Given the urgent need to prevent a potential humanitarian and climate crisis, finding solutions becomes paramount for humanity. However, the current situation on Earth poses a challenging dilemma: how can we simultaneously feed a growing population and mitigate climate change? Addressing this problem first requires a profound understanding of the drivers of climate change and the identification of potential strategies for climate mitigation (Falkowski et al., 2000; Grace, 2004).

The regulation of our climate is intricately linked to the transfer of C (referred to as C fluxes) between various reservoirs in the **global C cycle** (Post et al., 2000) (**Figure 1.3**). The C reservoirs differ in size, biogeochemical activity and sensitivity to anthropogenic impacts. Once, there existed a finely balanced global climate system, in which C cycled between the atmosphere, oceans, and terrestrial reservoirs through natural processes (dashed arrows in **Figure 1.3**). However, human activities, such as the burning of fossil fuels, deforestation, and land use change, have disrupted the previously existing equilibrium (Foley et al., 2005). These activities have caused substantial emissions of CO₂ into the atmosphere, exceeding the natural capacity of the C cycle to effectively absorb and regulate these emissions (Olofsson and Hickler, 2008). In total, an estimated 465 ± 25 petagrams (Pg) C ($1 \text{ Pg C} = 10^{15} \text{ g C} = 1.000.000.000 \text{ t C}$) of cumulative fossil CO₂ was emitted over the historical period from 1850 to 2021. During the 1960s, fossil CO₂ emissions were $3.0 \pm 0.2 \text{ Pg C yr}^{-1}$, increasing each decade up to $9.6 \pm 0.5 \text{ Pg C yr}^{-1}$ over the 2012-2021 period (**Figure 1.3**) (Friedlingstein et al., 2022).

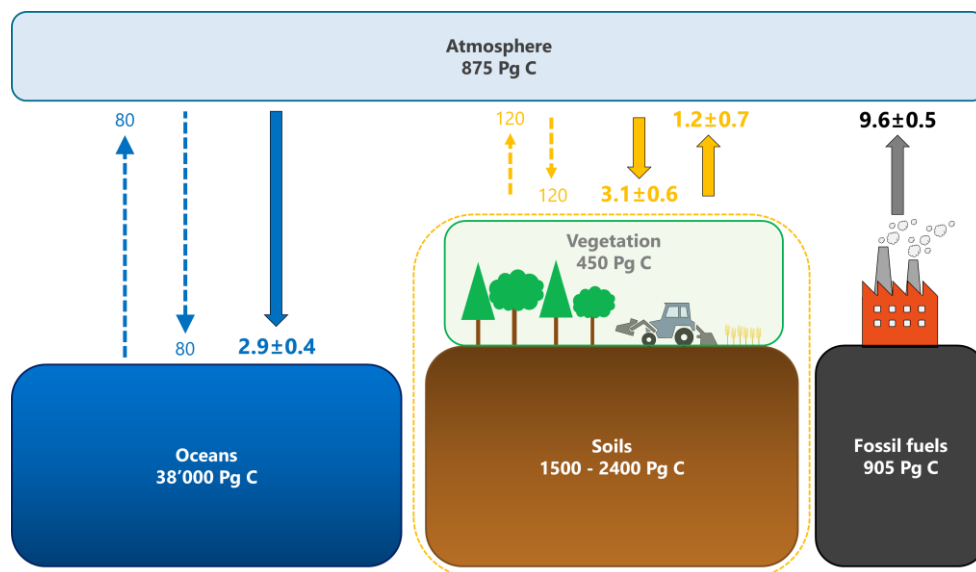


Figure 1.3: Simplified illustration of the main C reservoirs and C fluxes within the global C cycle for the period 2012-2021. Boxes represent the different C reservoirs with stocks given in Pg C. Arrows represent C fluxes and are given in Pg C yr⁻¹ ($1 \text{ Pg C} = 10^{15} \text{ g C} = 1.000.000.000 \text{ t C}$). The dashed arrows represent the natural fluxes and solid arrows represent anthropogenically caused fluxes. The numbers are taken from Friedlingstein et al. (2022), except for the soil C reservoir (Batjes, 2014; Scharlemann et al., 2014).

The associated increasing global temperatures trigger feedback mechanisms that further enhance the pressure on terrestrial C reservoirs (Hicks Pries et al., 2017; Melillo et al., 2017). For instance, increased global temperatures raise the risks of massive species extinctions, i.e., biodiversity loss (Foley et al., 2005; Thomas et al., 2004), which in turn will also affect humans due to changes in ecosystem functioning (Cardinale et al., 2012). In addition, climate-induced shifts in planting and harvest dates, and alternating weather extremes (Li and Fang, 2016; Nearing et al., 2004), can lead to severe soil erosion (Borrelli et al., 2020). Furthermore, elevated temperatures increase the mineralization of soil organic matter (SOM) (van Groenigen et al., 2014) - the storage medium of C in soil - that is already being depleted by poor agricultural management (see **Chapter 1.4**).

With an estimated total of 2416 Pg C in the upper 2 m (1505 Pg C in the upper 1 m and 704 Pg C in the upper 30 cm), **soils** represent the largest terrestrial C reservoir (Batjes, 2014; Scharlemann et al., 2014), storing more C than the vegetation and the atmosphere combined. C is stored in soils in the form of **SOM**. It refers to all plant- and animal-derived organic components present in the soil and occurs in a wide spectrum of decomposition stages, i.e., from fresh, undecomposed plant litter to highly decomposed microbial degradation products (Kögel-Knabner, 2002). It enters the soil through the transfer of atmospheric CO₂ via organic matter (OM), where it can be subsequently stabilized over extensive periods of time (see **Chapter 1.2**). This process, known as **C sequestration**, plays a crucial role in climate change mitigation through C withdrawal from the atmosphere (Sierra et al., 2021; Smith, 2016).

It is estimated that the potential climate-mitigating contribution of natural climate solutions, including the restoration and conservation of forests, wetlands, grasslands and agricultural lands, amounts to 23.8 Pg CO₂ equivalent yr⁻¹ (Griscom et al., 2017). About a quarter of this potential is attributed to soil C, of which 60% is accounted for by C restoration within degraded soils (Bossio et al., 2020). In addition, there is a high degree of C undersaturation, estimated globally at 58% within topsoils (Georgiou et al., 2022). Thus, increasing SOM stocks in soils creates biological C sinks, making soil C sequestration a negative emission strategy for climate change mitigation (Paustian et al., 2019). In practice, this can be achieved through targeted soil management, so-called climate-smart practices (Paustian et al., 2016) (see **Chapter 1.5**). Therefore, it is our responsibility to proactively optimize the role of soil as a crucial regulator of the global climate.

1.2. The SOM life cycle - from assimilation to mineralization or long-term storage

Besides their important role in C storage, the crucial factor for climate mitigation, soils offer a range of various ecological services that are vital for the functioning of ecosystems and essential for human well-being. These services, as categorized by the Millennium Ecosystem Assessment (MEA, 2005), include cultural services, the provision of food and fiber, support of nutrient cycling, biomass production, soil formation, habitat for biological activity, and water filtration. The soils' C content, i.e. amount of SOM, is a decisive factor for soil fertility, soil quality and soil health as a whole (Bünemann et al., 2018; Lal, 2016; Lehmann et al., 2020a), enabling the provision of the majority of ecosystem services (Adhikari and Hartemink, 2016).

SOM is a highly dynamic component of soil that is continuously being formed and decomposed (Kleber et al., 2015; Lehmann and Kleber, 2015; Schmidt et al., 2011). This results in a complex and diverse array of chemical compounds within different SOM fractions that vary in their stability, persistence, and reactivity (Christensen, 2001; Kögel-Knabner, 2002; Kögel-Knabner et al., 2008a; Lavalée et al., 2020). Knowledge about the distribution of SOM between these distinct fractions (Cotrufo et al., 2019) is steadily implemented in widely used ecosystem and climate models, which significantly contributes to the prediction of C fluxes within our global system (Dynarski et al., 2020; Wieder et al., 2013).

Under consistent climatic conditions, the long-term C flow equilibrium between constant OM inputs and losses establishes a distinct, site-specific SOM content (Sümmerer and Wiesmeier, 2023). OM is introduced into the soil after photosynthesis of atmospheric CO₂ via plants in the form of litter, crop residues, organic fertilizers (i.e. above-ground inputs), or root inputs (i.e. below-ground inputs) (**Figure 1.4**). OM loss as CO₂ from the soil to the atmosphere occurs primarily through mineralization (i.e., microbial respiration). In addition, SOM can be redistributed by processes such as soil erosion, resulting in losses via lateral redistribution (Chappell et al., 2015) and leaching to aquatic systems (Nakhavali et al., 2020) (not included in **Figure 1.4**).

Following its input into the soil, freshly added OM is present primarily in an unprocessed, unaltered, and particulate form referred to as **free particulate organic matter (fPOM)**. It is characterized by high C/N ratios and its composition is dominated by chemically complex plant-derived compounds (e.g. lignin, cellulose, hemicellulose) (Lavalée et al., 2020). Depending on its intrinsic chemical recalcitrance (von Lützow et al., 2006), heterotrophic microorganisms such as bacteria and fungi, break down the readily available (i.e. labile) OM through enzymatic reactions and utilize it as a source of energy for their own growth and metabolic activities (i.e. maintenance), in a process called **decomposition**. The rate of

decomposition is influenced by factors such as temperature, moisture, and pH, with warmer, moister soils generally exhibiting faster rates of decomposition (Walker et al., 2018; Wang et al., 2016). OM decomposition results in the release of nutrients ready for plant take-up (**Figure 1.4**), and the secretion of microbial substances, which enhance the interaction between mineral and organic particles by serving as major cementing agents (Costa et al., 2018; Wagai et al., 2018). This enhances the formation and stability of mineral-organic clusters, called aggregates (Abiven et al., 2009; Kong et al., 2005), which facilitate soil structure formation (Chenu and Cosentino, 2011).

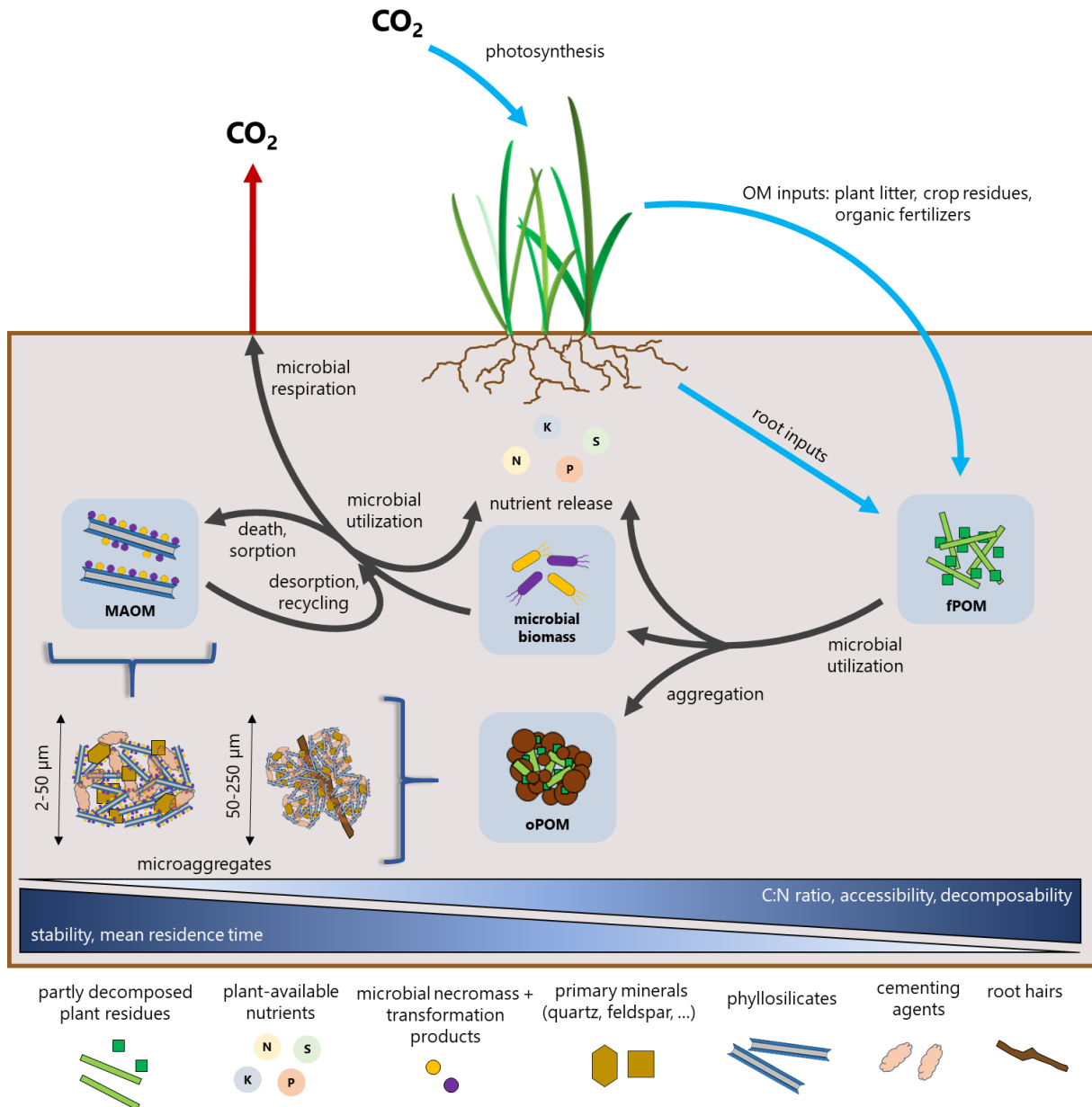


Figure 1.4: Schematic illustration of SOM formation pathways and stabilization mechanisms. The blue colored arrows show the fluxes/inputs of CO₂ or C from the atmosphere or biomass into the soil and the red colored arrow shows the loss of SOM via mineralization back into the atmosphere as CO₂. The black arrows represent the processes and mechanisms in the soil involved in SOM (de)stabilization described in the flow text. Own illustration, adapted from Dynarski et al. (2020), Liang et al. (2019), Meng et al. (2022) and Totsche et al. (2018).

Soil aggregates follow a hierarchical structure (Oades, 1984; Tisdall and Oades, 1982) (**Figure 1.4**). This encompasses the formation of microaggregates (<250 μm) within macroaggregates (>250 μm) (Balabane and Plante, 2004; Oades and Waters, 1991; Six et al., 2000). The OM within macroaggregates aggregates is referred to as **occluded particulate organic matter (oPOM)**. It is in an advanced stage of decomposition, but its incorporation into aggregates ensures a spatial separation from decomposers and enzymes, and thus leads to increased physical protection (Kögel-Knabner et al., 2008a). This is manifested in an increased stability and permanence, highly dependent on aggregate turnover, and therefore agricultural management practices (Poeplau and Don, 2013; Six et al., 2000). Aggregates can also further be stabilized via e.g. enmeshment of roots and fungal hyphae (Oades, 1984).

Continued POM decomposition involves the breakdown of complex organic compounds into simpler molecules (e.g. polysaccharides, proteins, lipids) via depolymerization (Kleber et al., 2021; Lavalley et al., 2020). Eventually, highly degraded SOM consists of a high proportion of microbial residue, so-called necromass and transformation products enriched in polar functional groups (Angst et al., 2021; Liang et al., 2019; Miltner et al., 2012; Sae-Tun et al., 2022; Zhou et al., 2023). Their increased aqueous solubility, chemical reactivity and smaller molecular size promote their stabilization as **mineral-associated organic matter (MAOM)** via adsorption onto fine mineral particle surfaces (fine silt and clay, <6.3 μm) and entrapment in micro-aggregated organo-mineral structures (Kleber et al., 2021; Totsche et al., 2018). These stabilization processes increase the turnover times of MAOM up to hundreds to thousands of years (Cotrufo et al., 2015; Kleber et al., 2015; Lavalley et al., 2020; Six et al., 2002; von Lützow et al., 2006), giving it the notion of a stable C pool. As a result, the prevailing concept emerged, that soils containing high amounts of fine-sized minerals with large surface areas (e.g. phyllosilicates) have a higher capacity for long-term storage of SOM (Feng et al., 2013; Hassink, 1997; Stewart et al., 2007). However, only recently has the reversibility of these mechanisms been observed by priming via root exudates (Jilling et al., 2021; Keiluweit et al., 2015). This ensures the re-introduction of MAOM into the active SOM cycle, where it is subject to quick microbial assimilation or re-stabilization, adding another dynamic aspect to the system (**Figure 1.4**).

Separation of these operationally defined POM and MAOM fractions via density and particle size differences (physical fractionation, see **Chapter 2.2.3**) (Just et al., 2021; Leuthold et al., 2022; Poeplau et al., 2018; von Lützow et al., 2007), allows us to illuminate management-induced effects on long-term and short-term C sinks in soil. Furthermore, employing specialized analytical tools (as described in **Chapter 1.3**), allows for a more profound understanding of the highly complex and dynamic microbially fueled mechanisms involved in the stabilization and destabilization of SOM. This process-based understanding will ultimately help improve biogeochemical and climate models to make predictions about C cycling under future climate.

1.3. Analytical tools as a driving force in elucidating SOM stabilization mechanisms

The present state of knowledge about the functionality and dynamics of different SOM fractions and the underlying stabilization mechanisms has been fueled by the steady development and improvement of analytical approaches over the last decades. The following sections describe the state-of-the-art analytical tools, their underlying principles, and their relevance to SOM research that have been used in this work and are relevant to future research (see **Figure 1.5**).

The **BET** method for measuring the **specific surface area** (SSA) of solid materials was developed by chemists Stephen **B**runauer, Paul Hugh **E**mmett and Edward **T**eller in 1938 (Brunauer et al., 1938). SSA refers to the total surface area of a solid material per unit of mass ($\text{m}^2 \text{g}^{-1}$). This measure is important since the dominant mechanism responsible for the formation of stable organo-mineral associations in soil is adsorption of plant- and microbial-derived organic compounds on clay and fine-silt surfaces (Abramoff et al., 2021) (e.g. via ligand exchange, cation bridging or van der Waals forces (Gu et al., 1994; Heister, 2014; Yeasmin et al., 2014)).

The BET method uses the principle that surfaces of solid materials offer numerous reactive sites, enabling the take-up of certain volumes of gas via physisorption (Totsche et al., 2010). For analysis, nitrogen gas (N_2), used as the adsorbate, is gradually introduced into the sample cell and relative gas pressures are changed until saturation. The amount of N_2 adsorbed as a monolayer to the surface of the solid under various pressures (i.e. gas adsorption isotherm) (Sing, 1995) at constant temperatures (77 K) can be quantified and the SSA of the sample determined. This provides information on C loading, a useful measure for the degree of C saturation, stability and potential C sequestration of the analyzed fine mineral soil fraction (Feng et al., 2014; Schweizer et al., 2021).

Radiocarbon dating is a method based on the principle of radioactive C isotope decay that helps scientists determine the age of organic materials. It was developed in the late 1940s by a team of scientists led by the chemist Willard Libby, inspired by the work of physicist Serge Alexander Korff, who discovered the formation of ^{14}C . On Earth, ^{12}C makes up the vast majority (98.93%) of all C found, followed by ^{13}C (1.07%) (Hoefs, 2009). These two C isotopes are stable, which means they are not subject to decay. ^{14}C has two additional neutrons in its nucleus, making it unstable and thus subject to radioactive decay with a half-life of approximately 5730 years (Trumbore et al., 2016). It is a cosmogenic radionuclide, which occurs only in trace amounts in the environment and is constantly being formed naturally in the upper stratosphere by the interaction of cosmic rays with N atoms. After oxidation to $^{14}\text{CO}_2$, it mixes into the global C cycle to establish an equilibrium.

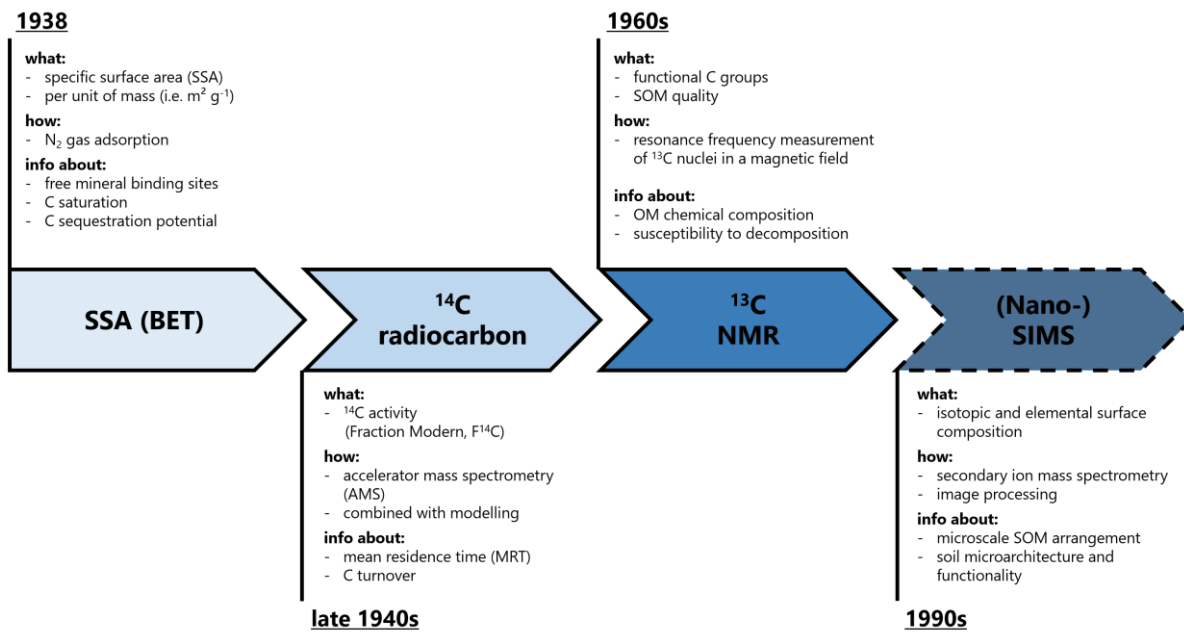


Figure 1.5: Overview of some key technologies and analytical approaches used in this thesis that have greatly benefited understanding of the processes involved in SOM cycling. The dashed "NanoSIMS" technology was not used in this thesis, but is important for further insight into mechanisms that occur at the sub-micron scale.

However, the massive number of nuclear bomb tests conducted primarily by the United States and the Soviet Union between 1945 and 1963, resulted in the substantial emission of 'bomb ^{14}C ' and a characteristic increase in its atmospheric concentration (' ^{14}C bomb peak'). Plants take up the atmospheric ^{14}C during photosynthesis and incorporate it into their biomass, where it slowly decreases according to the radioactive decay law. Consequently, the ^{14}C concentration within dead plants and their decomposition products in the soil reflects the atmospheric ^{14}C concentration at the time of their death, making 'bomb ^{14}C ' an ideal biological tracer (Stenhouse and Baxter, 1977). Using accelerator mass spectrometry (AMS), the ratio of radioactive ^{14}C to the stable ^{12}C and ^{13}C within a sample can be measured and compared to the known atmospheric ratio at a particular time (usually defined as the year 1950). The result is reported as $F^{14}\text{C}$ ('Fraction Modern') and expresses the ^{14}C activity within the analyzed sample (Trumbore et al., 2016). For soil scientists, these data are particularly useful for C modelling because they provide valuable information about the intrinsic time scales specific SOM fractions cycle, from which SOM mean residence times (MRT) and C turnover can be derived (Sierra et al., 2017; Wang et al., 1996) (see **Chapter 3.3.3 & 3.3.4**).

Solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy is a technique used in organic geochemistry to investigate the molecular composition of solid samples, such as the highly heterogeneous structural components of SOM (Kögel-Knabner, 1997). This technique was developed and refined between the 1960s and 1980s and was first used to characterize the structural composition of humic substances (Barton and Schnitzer, 1963). Later, analysis of bulk soils was accomplished (Wilson et al., 1981), which paved the way for the characterization and quantification of different OM inputs

(Kögel-Knabner, 2002). This technique also provides valuable information about the chemical bonding and functional groups present in the analyzed solid samples (e.g. ground POM, MAOM) (see **Chapter 2.3.2.3.**). ^{13}C NMR spectroscopy takes advantage of the fact that certain atomic nuclei respond with a nuclear spin upon the application of an external magnetic field. Because of its odd number of nucleons (6 protons + 7 neutrons), ^{13}C has a nuclear spin. The magnetic field is generated by an NMR spectrometer, which applies a series of radio-frequency pulses to the sample that correspond to the resonance frequency of the ^{13}C nuclei. The cross-polarization magic angle spinning (CPMAS) technique allows the magnetic polarization to be transferred from a strongly polarized atom to an adjacent atom. Magic-angle spinning is used to rotate the sample at a specific angle (54.74°) to the magnetic field axis, which homogenizes the signal and improves spectral resolution (Polenova et al., 2015). The NMR spectrometer measures the amount of energy absorbed to resonate the nucleus of an atom, which allows for the differentiation between nuclei on the basis of characteristic resonance frequencies (Knicker, 2011). The resonance frequency of each ^{13}C nucleus is compared to a reference molecule (tetramethylsilane) in an NMR spectrum (i.e. chemical shift) (see **Figure S2.1**).

Overall, NMR spectroscopy provides a qualitative assessment of SOM, allowing the analysis of the chemical composition and structural characteristics of organic compounds present in soils. The application of NMR spectroscopy has greatly contributed to our understanding of SOM dynamics, nutrient cycling, and the effects of different management practices on soil functioning.

Secondary ion mass spectrometry (SIMS) is a technique used for surface analysis of solid samples. **NanoSIMS**, short for **nanoscale secondary ion mass spectrometry**, is a high-resolution imaging technique, optimized for SIMS imaging. It enables the study of isotope ratios and elemental composition of solid materials at the sub-micron scale, i.e. the soil process scale (Mueller et al., 2022; Mueller et al., 2013), which has significantly expanded the horizons of the observable domain of soil science (Heister et al., 2012; Herrmann et al., 2007). The technique was developed in the 1990s, and with nowadays around 50 instruments in use worldwide, the NanoSIMS 50 (or 50L) (CAMECA, France), conceived by the French physicist Georges Slodzian (Slodzian et al., 1992) and designed by Bernard Daigne, François Girard and François Hillion (Hillion et al., 1993), is the leading instrument for the conduction of NanoSIMS measurements. Briefly, NanoSIMS analysis is a destructive process, where the surface of the solid material to be analyzed is bombarded with a high-energy ion beam of Cs^+ or O^- primary ions, focused by a coaxial lens (Herrmann et al., 2007; Mueller et al., 2013). This results in the ejection of secondary ions ($\text{Cs}^+ =$ negative ions, $\text{O}^- =$ positive ions) of the upper sample surface in a process called sputtering. This secondary ion beam is then focused and directed into the detection system of the instrument, consisting of an electrostatic and magnetic sector (i.e. double-focusing design) (Nunez et al., 2017). Here, ejected ions are separated in a mass spectrometer with a high mass resolution, according to their mass-to-charge ratios (Cs^+ : e.g. $^{12}\text{C}^-$, $^{13}\text{C}^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^{15}\text{N}^-$, $^{28}\text{Si}^-$, $^{27}\text{Al}^{16}\text{O}^-$, $^{56}\text{Fe}^{16}\text{O}^-$; and O^- : e.g. ^{23}Na , ^{39}K , ^{44}Ca , ^{56}Fe).

The application of NanoSIMS in soil science provided detailed insights into SOM sorption mechanisms (Vogel et al., 2014) and the microscale arrangement of MAOM (Keiluweit et al., 2012; Schweizer et al., 2021). It also enabled the visualization of SOM formation pathways (Vidal et al., 2021) and the identification of functional microdomains as the smallest building blocks of soils controlling SOM sequestration and stabilization (Steffens et al., 2017). NanoSIMS analysis was not included in this thesis, but its importance for process understanding of SOM dynamics is undisputed.

1.4. Agriculture - a history of intensification and degradation

For millions of years, our early ancestors relied solely on the resources provided by the natural environment for foraging. However, favored by the end of the Younger Dryas cold period about 10'000 to 12'000 years ago (Montgomery, 2007), the cultivation of crops and domestication of animals led to the first forms of agriculture (Zeder, 2011). This so-called **Neolithic Revolution**, enabled a more reliable source of food and induced a shift from the people's nomadic hunter-gatherer to sedentary lifestyles, i.e. "from foraging to farming" (Weisdorf, 2005). Based on local knowledge, traditional but resource-limited farming practices gradually developed. This form of agriculture was largely sustainable because it focused on maintaining soil fertility and adapting to natural rhythms. Over thousands of years, advancements in farming equipment and practices were made, including the invention of the hand-held plow (Pryor, 1985) and first irrigation systems (Gulhati and Smith, 1967), which increased agricultural productivity. This led to a significant transformation of natural ecosystems into expansive agriculturally used territories, and triggered the emergence of complex societies, cultures and ultimately fostered the rise of modern civilizations (Olsson and Paik, 2016; Weisdorf, 2005).

After millennia of farming, accompanied by the first real cropland expansion (**Figure 1.6**), the **Second Agricultural Revolution** took place between the mid-17th and late 19th century as a response to the increasing food demand of the growing population. It started in Britain and later expanded to other Western European countries, and eventually spread into the rest of the world. This period was marked by a rise in agricultural productivity, efficiency (Allen, 1999) and massive expansion (**Figure 1.6**), sparked by the implementation of agricultural practices (e.g. crop rotations), and tools (e.g. mechanical seed drill and steel plow), and the privatization of cropland (Sullivan, 1985). The increased agricultural productivity massively contributed to economic growth and is therefore believed to have played a significant role in the emergence of the Industrial Revolution that followed (Patriquin, 2004). This in turn marked the start of the so-called Anthropocene (Crutzen, 2002), i.e. the age of fossil fuel exploitation, GHG emissions, deforestation and environmental pollution (Steffen et al., 2011).

The Third Agricultural Revolution, also known as the **Green Revolution**, was a period between the 1960s and 1980s, characterized by high rates of investment, research and technological innovations in agriculture (Evenson and Gollin, 2003). Mainly motivated by the need for increased food production in developing countries, especially in Asia and sub-Saharan Africa, great success was achieved in the breeding of robust and high-yielding wheat and maize varieties (Evenson and Gollin, 2003; Khush, 2001). In addition to the positive effects of increased food production and reduced famine, particularly in Asia (Eliazer Nelson et al., 2019), this industrialization of agriculture also brought about negative effects on the environment. Most notably, cropland expansion and the introduction of policies to promote rapid

agricultural intensification (Pingali, 2012) led to a massive increase in the use of chemical fertilizers, synthetic herbicides and pesticides (Dethier and Effenberger, 2012), which resulted in environmental pollution by runoff (Pingali, 2012). In addition, the increased focus on high-yielding crop varieties led to a reduction in crop diversity. This resulted in the neglect of organic inputs in favor of synthetic fertilizers to provide crops with essential nutrients for rapid growth, and ultimately losses of soil fertility. Furthermore, increased tillage led to increased soil degradation via erosion (Singh, 2000).

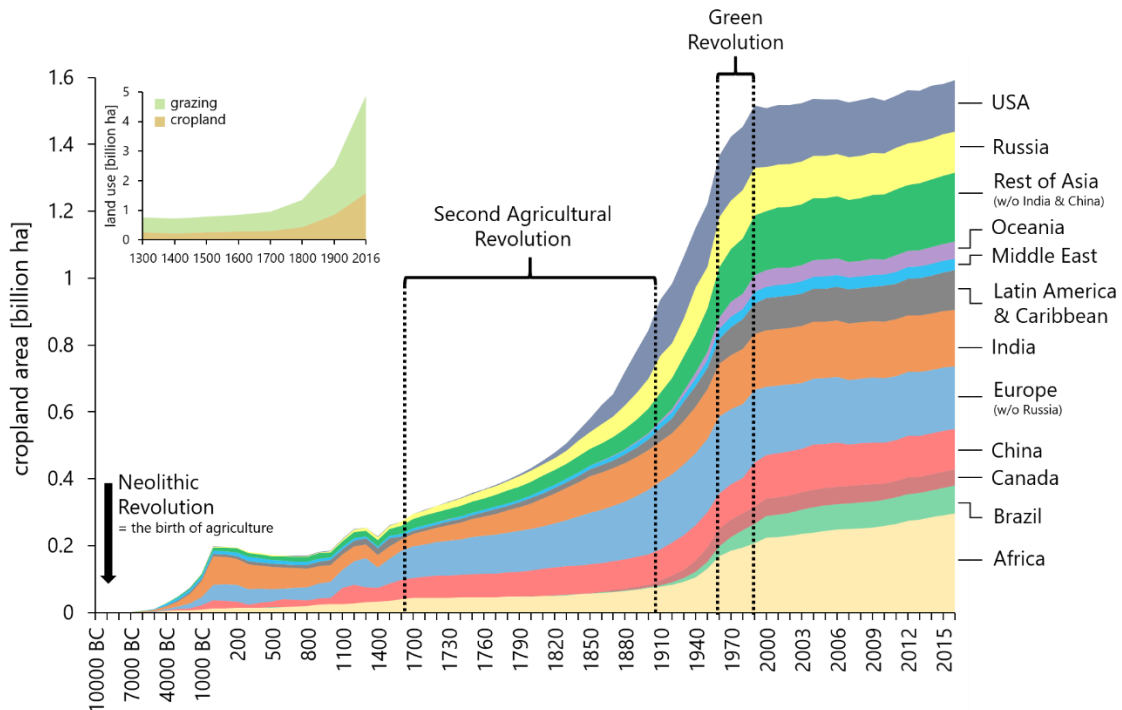


Figure 1.6: Historical development of global cropland area expansion (i.e. arable land and permanent crops) from the beginnings of agriculture (ca. 10000 BC) until present. The numbers are given in billion ha, and the crucial periods in agricultural development are indicated with brackets. At the top left, the development of the total area used, divided into arable and pasture land, is shown as a rough overview from 1300 until present. This figure was redrawn and modified based on data from Ritchie and Roser (2013).

In response to the severe environmental pollution caused by the intensified agriculture, the 1970s saw a worldwide upsurge in the **organic farming movement** to combat soil degradation, restore soil fertility and ensure ecosystem services (Reganold and Wachter, 2016). Organic agriculture sets itself apart from conventional agriculture primarily through the ban of agrochemicals (i.e. synthetic fertilizers, herbicides, and pesticides). This reduces the pollution of soils, groundwater and the surrounding environment (Pimentel et al., 2005; Tilman, 1998). In addition, the enhanced application of organic fertilizers, as well as the increased input of crop residues, promote soil fertility through increased SOM contents (Gattinger et al., 2012), which helps developing a good soil structure (Shepherd et al., 2002). Furthermore, organic soil management promotes biodiversity (Bengtsson et al., 2005), biological activity (Lori et al., 2017; Mäder et al., 2002), increases the water retention (Lal, 2020), and improves nutrient availability for plants, all of which can lead to improved soil quality and soil health in the long term (Lal, 2015; Lehmann and Kleber, 2015).

Today, agricultural production (land use change excluded) contributes 10-12% (5.0-5.8 Pg CO₂ eq yr⁻¹) of global annual GHG emissions (mainly methane (CH₄) and nitrous oxide (N₂O)) (Smith et al., 2014) and the global land area used for agricultural purposes (i.e. cropland and grazing) (see top left in **Figure 1.6**) accounts for approximately 4.7 billion ha (FAO, 2021). It is estimated that between 1960 and 2019 alone, approximately one third of the global land area has been impacted by land use change (FAO, 2021; Winkler et al., 2021). This land use change has caused depletion of SOM (Poeplau and Dechow, 2023), with a total loss of 133 Pg C from soils since 1850 (Sanderman et al., 2017), thus contributing to climate change. If we continue to manage our soils in this unsustainable way, it could take as little as 60 years to lose all global topsoil (Arsenault, 2014).

The most radical, yet effective solution to restore soil C stocks and guarantee ecosystem services, would involve the total cessation of agricultural activities (Bell et al., 2023). However, this is not an option, as today globally 98.8 % of the daily calorie consumption is provided by agricultural systems that heavily rely on soil (Kopittke et al., 2019). Therefore, to repay our soil C "debts" (Sanderman et al., 2017), we need to find climate-smart solutions (Paustian et al., 2016) that prioritize sustainable management practices, contributing to climate mitigation via C sequestration. In this context, it is of utmost importance to understand how different management practices and fertilization schemes affect the formation and stabilization of SOM for long-term storage in managed cropland soils. A description of available practical measures, as well as political and financial initiatives ready to address this problem can be found in the following **Chapter 1.5**.

1.5. Taking action - incentives and measures for SOC build-up

In the wake of the human-induced and dramatically changing climatic situation of the past decades, it is of high importance and urgency to implement ways to reduce GHG emissions and identify sinks for atmospheric CO₂. In 2015, the United Nations Framework Convention on Climate Change (UNFCCC) **Paris Agreement** was adopted at the 21st UN Climate Change Conference (COP21) and has the goal of **limiting global warming to +1.5 to +2°C above pre-industrial levels** (UNFCCC, 2015), to prevent severe and irreversible impacts on the planet. In total, 196 nations voluntarily committed to pursuing this goal, which marks a milestone in international efforts to combat climate change and adapt to its effects.

Despite the slowdown in global fossil CO₂ emission growth rates over the past decade (Friedlingstein et al., 2022), this is still far from the emission reductions needed to meet the temperature targets set in the Paris Agreement. To intensify the efforts of limiting global warming, the European Union (EU) adopted the **European Green Deal**. It is a new growth strategy with the goal of transforming the EU into a resource-efficient society with **net zero GHG emissions by 2050** (EC, 2019), which would make Europe the first climate-neutral continent. A key point to consider in pursuit of climate mitigation is the inclusion of emissions from the agricultural sector. Failing to do so would impede the achievement of the desired 2°C target and lead to increased mitigation costs in other sectors (Reisinger et al., 2013; Wollenberg et al., 2016).

In the course of the 21st Conference of the Parties (COP21), the French government launched the voluntary action plan **"4 per 1000: Soils for Food Security and Climate"** ('4p1000'), which promotes soil C accrual to offset global anthropogenic CO₂ emissions (Chabbi et al., 2017; Minasny et al., 2017; Soussana et al., 2019). This initiative is based on the assumption that a 4‰ or 0.4% annual increase in global SOC stocks in the upper 30-40 cm (excluding permafrost) through improved climate-smart soil management (Paustian et al., 2016), would help largely counterbalancing human-induced CO₂ emissions. This initiative also promotes the collaboration among scientists, policy makers, practitioners and stakeholders (Rumpel et al., 2020). In addition, it emphasizes the key role of sustainable agricultural measures that contribute to SOM maintenance and accumulation, putting soils as C sinks at the center for combating climate change and ensuring food security. However, the feasibility of this aspirational initiative is intensively debated and repeatedly questioned in the scientific community (e.g. Baveye et al. (2018); Bruni et al. (2021); de Vries (2018); Martin et al. (2021); Poulton et al. (2018)), mainly due to discrepancies between theoretical and technically feasible C sequestration potentials.

Despite the growing knowledge within the scientific community and recognition of the central role of agriculture in climate change mitigation through SOC management on the political level and the public,

incentives for farmers are needed in order to achieve widespread practical implementation. These incentives are provided in the form of CO₂ certificates, also known as **C credits**. They refer to a private market-based funding mechanism that provides economic incentives for farmers to engage in **C farming**, i.e. in the implementation of agricultural practices that target SOC stock increases (Paul et al., 2023; Tang et al., 2019). The basic principle is as follows: A farmer voluntarily commits to building up SOC through C farming practices. The certifying initiatives approach the farmers and conduct an initial analysis of their soil. After a few years, a resampling is conducted and C credits are awarded to the farmer in case of increased SOC stocks. Eventually, CO₂ emitters (e.g. companies) can purchase C credits to offset their own emissions with SOC built up by farmers, thereby funding C reduction projects, rewarding farmers, and supporting C farming practices. There is a variety of **available C farming practices** that have been shown to re-store, maintain and increase C sequestration in agricultural soils (**Table 1.1**).

Table 1.1: Selection of C farming practices and their effects on SOC storage.

Practice	Effects on SOC storage	References
Organic fertilization (manures, composts)	<ul style="list-style-type: none"> Higher SOC stocks in organically managed soils compared to conventionally managed soils Higher SOC (9 t ha⁻¹) with compared to without FYM addition in soils of European field trials 	Gattinger et al. (2012) Körschens et al. (2013)
Crop residue management	<ul style="list-style-type: none"> Increased residue incorporation may increase SOC of European croplands by 19-23% over 50-100 years, under different climate scenarios Residue restitution led to an increase in stable SOC compared to residue export over 42 years 	Haas et al. (2022) Trigalet et al. (2014)
Improved crop rotations (cultivation of perennial forage crops, cover crops, intercropping)	<ul style="list-style-type: none"> Higher C sequestration rate (184 ± 86 kg C ha⁻¹ yr⁻¹) in intercropping compared to sole crop systems (0-20 cm) Mean increase of SOC by 2.8 t ha⁻¹ yr⁻¹ under perennial forage legumes Significantly higher SOC stocks under cover crops compared to reference croplands (C sequestration rate of 0.32 t ha⁻¹ yr⁻¹ over 54 years) Cover crops would lead to C sequestration rates of 0.28-0.33 t ha⁻¹ yr⁻¹ over a span of 50 years 	Cong et al. (2015) Guan et al. (2016) Poeplau and Don (2015) Seitz et al. (2022)
LUC from cropland to grassland	<ul style="list-style-type: none"> C sequestration rate of 1.01 t ha⁻¹ yr⁻¹ after LUC from cropland to grassland 	Conant et al. (2001)
Reduced tillage (RT) or no tillage (NT)*	<ul style="list-style-type: none"> RT increased SOC stocks by 3.8 t ha⁻¹ (0-15 cm) compared to plowing NT increased SOC stocks by 4.6 t ha⁻¹ (0-30 cm) compared to conventional tillage 	Krauss et al. (2022) Haddaway et al. (2017)
Agroforestry systems	<ul style="list-style-type: none"> C sequestration potential of 0.21 ± 0.79 t ha⁻¹ yr⁻¹ in the temperate zone 	Mayer et al. (2022b)

*note: RT and NT only lead to increased SOC in the uppermost soil layers, compared to conventional tillage. Due to the lack of plowing, the input of OM into deeper soil layers is lower. Overall, RT and NT provide increased erosion protection and thus reduced SOC losses.

Strict **criteria** have to be met to receive C credits for engaging in SOC build-up via C farming practices (Leifeld et al., 2019; Paul et al., 2023; Smith et al., 2020; Thamo and Pannell, 2016; Wiesmeier et al., 2020). The first priority is the need for **quantification and verification** of SOC stock changes caused by C farming practices. This requires an initial baseline sampling and a resampling after 3-5 years, since measurable SOC changes occur very slowly (**Figure 1.7**). In addition, a control must always be sampled as a reference to ensure that SOC changes are management-induced. Furthermore, the requirement of **additionality** must be met, meaning that SOC build-up should result exclusively from activities motivated by C credits (**Figure 1.7**). Measures that are carried out anyway as part of good professional practice, are not rewarded. Another criterion is the avoidance of shifting effects, so-called **leakage**. This would be the case if SOC build-up through C farming practices at one site, e.g. via compost application, comes at the expense of SOC losses at another site, such as biomass export for compost production from outside the land unit boundaries (Olson, 2013).

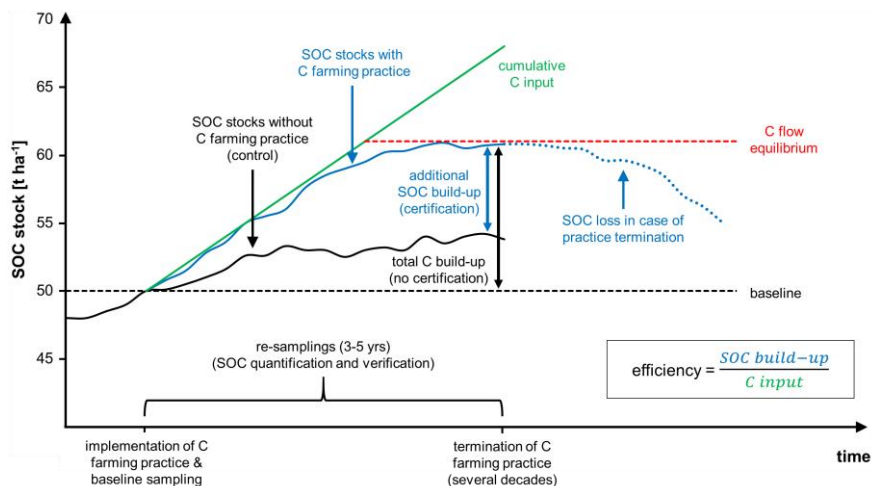


Figure 1.7: Schematic representation of the influence of increased C input through C farming practices on SOC stocks. The values shown on the y-axis and SOC stock trajectories are fictional, but represent realistic scenarios. The solid black and blue lines show SOC stock trends "business-as-usual" and affected by the C farming practice, respectively. The green solid straight line shows the cumulative C input (e.g. compost application). The dashed black and red lines represent the SOC stock before the start of the practice and the new equilibrium, respectively. The blue dotted line shows the potential SOC loss after termination of the practice. This figure was adapted from Wiesmeier et al. (2020) and Axel Don, Thünen Institut of Climate-Smart Agriculture.

Probably the most important and difficult criterion to meet for climate change mitigation is the **permanence** of the created soil C sink. SOC build-up is only effective if CO₂ is permanently removed from the atmosphere and stored in the soil as SOM. In this context, it is important to note, that the build-up of SOC is finite. Following an initially strong and efficient SOC increase after the start of the C farming practice, build-up efficiency decreases after a certain period (typically a few decades), since increased SOC stocks entail increased SOC turnover. Consequently, a new C flow equilibrium is established in the soil (**Figure 1.7**). In order to avoid the loss and ensure the permanent positive climate mitigating impact of this created C sink, a permanent commitment of the farmer to the continuation of the farming practice, even after reaching the new equilibrium, is indispensable.

1.6. Long-term experiments as scientific platform - the DOK trial

Many impacts and changes caused by certain management practices are simply not detectable over short time periods. Therefore, the validity of short-term experiments for a holistic view of farming systems and their impact on the environment is inadequate (Riar and Bhullar, 2020). Accurate assessment of the effects of management practices, such as changes in SOC, therefore requires consistent and well-documented long-term monitoring that typically spans decades (as depicted in **Figure 1.7**).

Long-term experiments (LTEs), with its periodically sampled permanent plots play a critical role as a platform where scientists and practitioners can interact, share information, test scientific ideas and practical implementation approaches (Richter et al., 2007). They are used for the assessment of farming practice impacts, on soil quality (Bai et al., 2018), nutrient management (Miao et al., 2011), crop production (Johnston and Poulton, 2018), and the environment as a whole (Rasmussen et al., 1998). In addition, they are used for teaching and demonstration, i.e. dissemination. Ultimately, LTEs serve as a valuable platform for collaboration and knowledge exchange and their results serve the evidence-based decision-making to establish sustainable agricultural practices for climate mitigation.

Particular challenges of LTEs are mainly the extensive and coordinated planning and evaluation, as well as the long duration until usable, meaningful data are available and the subsequent, which poses the risk of neglecting the experiment (Richter et al., 2007). The number of LTEs conducted worldwide is possibly in the hundreds, if not thousands, with around 600 running for more than 20 years (Grosse et al., 2020; Körschens, 2006). They have produced a vast output of scientific publications, significantly contributing to our understanding of farming practices and their impacts on soil and the surrounding environment. A few selected well-known representatives are listed in **Table 1.2**.

Table 1.2: Selection of famous worldwide long-term experiments.

Field trial	Location	References
LTEs at Rothamstead Research	Harpenden (Hertfordshire, UK), initiated in 1843	Macdonald et al. (2020)
Farming systems trial at Rodale Institute	Kutztown (Pennsylvania, USA), initiated in 1981	Pimentel et al. (2005)
Continuous field trial Eternal Rye	Halle (Saxony-Anhalt, D), initiated in 1878	Merbach and Deubel (2007)
Askov fertilization trial	Askov (Jutland, DK), initiated in 1894	Christensen et al. (2022)
Static fertilization experiment	Bad Lauchstädt (Saxony-Anhalt, D), initiated in 1908	Körschens et al. (1994)
The DOK system comparison trial	Therwil (Basel-Landschaft, CH), initiated in 1978	Mäder et al. (2002)

For this thesis, the **DOK system comparison trial** is the focus of research. It is a long-term field experiment, initiated in 1978, that compares bioDynamic, bioOrganic and Konventionell (German for conventional) farming systems (Mäder et al., 2002). It is jointly managed by the Research Institute of Organic Agriculture, FiBL (Frick, canton of Aargau) and the Federal Swiss Institute for Agricultural Research, Agroscope (Reckenholz, canton of Zurich).

The DOK is situated 300 m above sea level, about 10 km south of the city of Basel, between the villages Therwil and Biel-Benken in the Canton of Basel-Landschaft, Switzerland (7°32' E, 47°30' N) (**Figure 1.8**). It is located at the end of the Faltenjura, the folded part of the Jura, a subalpine mountain range north of the Western Alps. This region marks the southwesternmost end of the Upper Rhine Valley, which formed in the early Cenozoic, late Eocene (56-34 Ma before present). The hills surrounding the DOK trial consist of limestone in the south and molasses freshwater sediments in the north slope. The small valley (= Leimental) is formed by two small streams cutting into Pleistocene loess sediments. During the Pleistocene, periglacial processes led to a colluvial accumulation of eroded material (limestone block in profile) and windblown loess material. Soil formation has taken place over the past 10,000 years, with possible intermittent periods of erosion or accumulation processes. The region is characterized by its mild climate, with mean annual temperature of 10.5°C and mean annual precipitation of 842 mm. This, allows an effective vegetation period of 210-215 days per year (Krause et al., 2020).

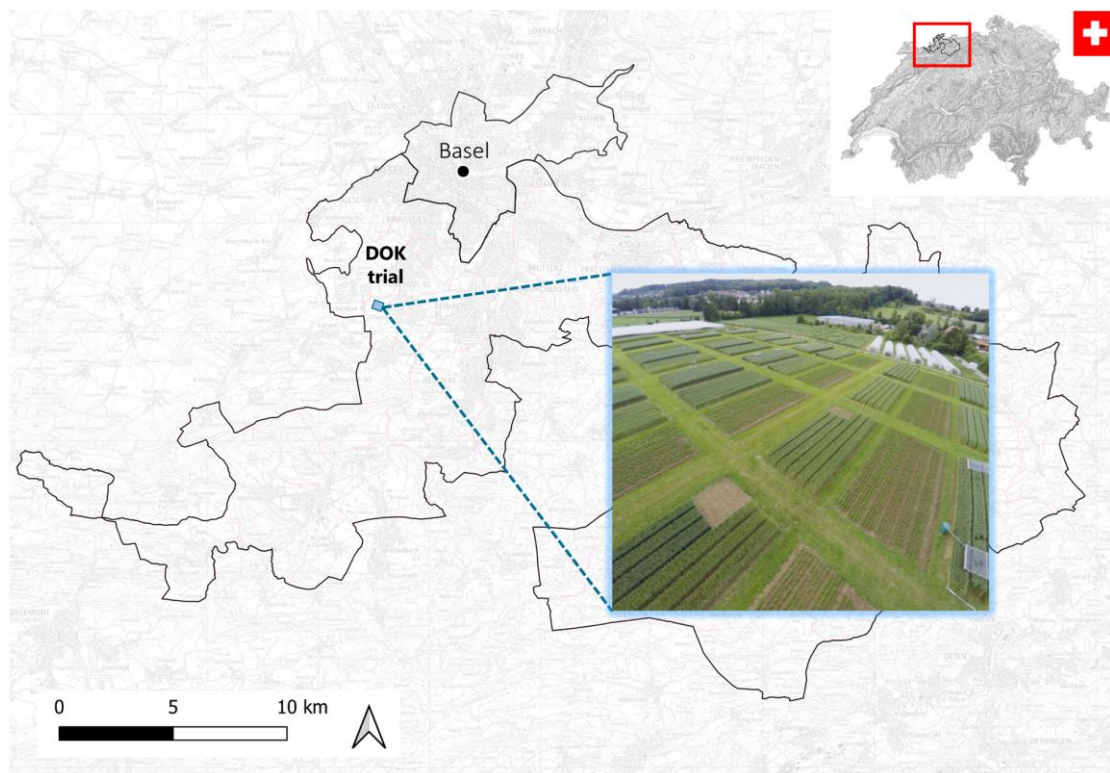


Figure 1.8: Location of the DOK long-term trial in northwestern Switzerland, in the canton of Basel-Landschaft, near the city of Basel. Adapted from Preisig et al. (2023). Photo: Tibor Fuchs.

The soil type is a Haplic Luvisol of loess material with a silty texture of 3% sand, 76% silt and 21% clay. It is characterized by an Ap horizon rich in OM, followed by a clay depleted illuvial horizon and a typical clay-enriched Bt horizon (**Figure S1.14**). This sequence typically occurs when clay is flushed downward by water and accumulates at greater depths in the soil (i.e. lessivage) (Quénard et al., 2011). The soil profile is free of carbonates; however, limestone as well as red brick fragments appear in the profile. In addition, up to pea-sized iron-manganese concretions (Childs, 1975) are present in the soil (**Figure S1.13 & S1.14**), but no distinct pattern of reduced conditions. Therefore, waterlogged conditions do not appear to be prevalent.

A special feature of the DOK system comparison trial is its extensive soil sample archive at the Federal Swiss Institute for Agricultural Research, Agroscope in Reckenholz. Here, the soil samples taken since the beginning of the experiment are stored and their allocation to scientists for research purposes is managed. Access to these decades-old samples from soil under well-documented and contrasting agricultural management, is an important cornerstone for the detailed observation and precise assessment of farming system impacts on the dynamics of SOC. Of particular importance is the duration of this field trial, which now covers a period of 44 years. This allows not only the investigation of short-term, i.e. seasonal, but also of long-term management-induced impacts on a large spectrum of soil parameters.

For an overview of the experimental design and the analyzed farming systems in focus of this theses see **Figure S3.1** and **Table 2.1**, respectively. They are introduced and described in the *Materials and Methods* sections of **Chapter 2 & 3**.

1.7. Thesis outline and objectives

The overarching objective of this thesis is to improve our understanding of how various farming systems impact SOM and, in turn, the soil's capacity to contribute to climate change mitigation. Using the analytical tools described in *Chapter 1.3*, I aimed to shed light on the mechanisms and dynamic aspects of C sequestration involved and underlying this process.

Despite the large number of studies conducted within the DOK trial, no study to date has conducted the long-term observation of farming system impacts on distinct fractions of SOM with different functionalities. Therefore, the objective of **Chapter 2** was to examine the impacts of farming systems with varying types and quantities of added fertilizers on these SOM fractions, over a 36-year period. By employing physical fractionation on archived soil samples from four different farming systems, I was able to separate SOM fractions with different stabilities. The fractionated samples were taken from 1982-2017, allowing for a quantitative analysis of the temporal dynamics of SOM, within and between these fractions. In addition, I used solid-state ^{13}C NMR-CPMAS spectroscopy to elucidate potential management-induced impacts on SOM quality in separated fractions across the farming systems. Furthermore, this study aimed to determine whether recommendations for soil management practices, that are beneficial for climate mitigation, could be derived from this long-term experiment.

In **Chapter 3**, the focus was on the finest physically fractionated, stable SOM fraction ($<6.3\ \mu\text{m}$), which is associated with long-term C storage. Through ^{14}C radiocarbon analysis via AMS and subsequent modeling, I aimed to gain important information about the permanence of SOM within this fraction and if fertilization-induced (qualitative and quantitative differences) impacts can be identified. Furthermore, BET specific surface area measurements provided detailed insights into possible stabilization mechanisms of SOM with fine mineral surfaces in this fraction.

Finally, **Chapter 4** serves to jointly discuss the main results presented in *Chapters 2 and 3*, and to put them into a broader context. Based on this, the contribution of agricultural soils to climate change mitigation is evaluated and its possible implications for political action and soil management strategies are discussed in the light of future climate. Furthermore, limitations of this thesis are pointed out and possible focal points for future research are identified.

Overall, I aimed at generating outcomes that would not only improve our understanding of the C sequestration potential of agricultural soils, but also play a central role in evaluating the impact of agricultural practices on climate change mitigation. As a result, these findings can have significant implications for decision-making in policy and practice, as well as contribute to the development of optimized climate-smart soil management practices, ultimately leading to direct practical benefits.

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CHAPTER 2

Fertilizer quality and labile soil organic matter fractions are vital for organic carbon sequestration in temperate arable soils within a long-term trial in Switzerland

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Abstract

Agricultural management of soils has led to severe losses of soil organic matter (SOM), accompanied by an increased release of CO₂ into the atmosphere and a reduction of soil fertility. Especially under the aspect of global warming and the increasing demand for food, there is a need for sustainable management options increasing soil organic carbon (SOC) storage in agricultural soils, but knowledge gaps exist regarding C persistence in, and its transfer between functional SOC pools, within different farming systems. Here we report on impacts of different farming systems on the temporal dynamics of SOM fractions within the DOK long-term trial (Switzerland), from 1982 to 2017. A purely minerally (CONMIN), a minerally and organically (CONFYM), and a purely organically fertilized farming system (BIODYN) were compared with an unfertilized control (NOFERT). We separated archived soils from the Haplic Luvisol (0-20 cm depth) into particulate (POM) and mineral-associated OM (MAOM) fractions, via physical fractionation, and analyzed the chemical composition of selected fractions via solid-state ¹³C CPMAS-NMR spectroscopy. We demonstrate that under none of the analyzed farming systems, additional SOC was sequestered in the clay-sized MAOM fraction (<6.3 μm) over a period of 36 years. In all fertilized systems, the amount of SOC in this pool did not change, but strongly decreased in NOFERT (-27%). Bulk SOC increased in BIODYN (+13%) and CONFYM (+5%), but decreased in CONMIN (-8%) and NOFERT (-20%). As no additional SOC accumulated in the clay-sized MAOM fraction, this implies that bulk SOC increases were solely stored within labile POM fractions. NMR spectra showed comparable POM chemical compositions between different systems. Differences in fertilizer quality (BIODYN = composted farmyard manure vs CONFYM = stacked farmyard manure + mineral fertilizer) and the omission of pesticides resulted in better conditions for POM stabilization and consequently significantly higher C contents of occluded POM (oPOM) within aggregates, in BIODYN. However, this labile fraction is at high risk of being lost within a few days, as illustrated by the strong annual oPOM-C content fluctuations depending on the timing of soil sampling after harvest. The highest post-harvest oPOM-C losses in BIODYN indicate the higher dynamics compared to CONFYM. It is anticipated that only sustainable fertilization methods with continuous application of solely organic fertilizers in the long-run can maintain SOC in the labile POM fractions at elevated levels, thereby ensuring soil fertility. It also illustrates the need for prevention of major losses by careful management of the labile POM fractions, as this OM could associate with fine mineral particles at a later stage and thus contribute to OC sequestration in the stable SOC pool. Overall, the potential of arable soils to accumulate stable OC for long-term sequestration is questioned.

Keywords: physical fractionation, carbon dynamics, fertilization, manure, farming system comparison, organic farming

2.1. Introduction

The potential of agricultural soils to serve as a long-term carbon (C) sink is currently subject of intense debate at political and economic levels (Minasny et al., 2017; Rumpel et al., 2020) as a measure to take action against climate change and counteract soil degradation. However, land use change to and intensive use of arable land has led to considerable depletion of soil organic matter (SOM), which plays a key role in soil structure formation, plant nutrition and soil fertility (Bünemann et al., 2018; Dignac et al., 2017).

Soils act as C sink when organic C inputs are bigger than the losses by decomposition. Sequestration of such added C is achieved when it is stabilized and thus stored in the soil for a long time. “Climate-smart” agricultural management not only offers the opportunity to sequester atmospheric CO₂, it helps fostering key soil functions and therefore improving soil health (Lehmann et al., 2020a; Paustian et al., 2016; Smith, 2012; Smith, 2016). A variety of management options has been established aiming to enhance C inputs to agricultural soils. Organic matter (OM) input via manure (Gross and Glaser, 2021), improved crop rotations with legumes (Kumar et al., 2018), cover crops (McDaniel et al., 2014; Poeplau and Don, 2015), biochar application (Smith, 2016), agroforestry (De Stefano and Jacobson, 2018) and organic farming with grass-clover in the rotation (Jarvis et al., 2017) are prominent examples. In the soil, any OM is subject to decomposition and subsequent mineralization, stabilization through physical protection in aggregates or association with mineral soil particles (Kleber et al., 2015; Schmidt et al., 2011; Wiesmeier et al., 2019). During decomposition, its chemical composition is altered. Therefore SOM quality spans all levels of decomposition from fresh, undecomposed and structurally complex plant litter to highly processed organic molecules (Kögel-Knabner, 2002). These forms are characterized by variable turnover rates (Christensen, 2001; Kölbl and Kögel-Knabner, 2004).

Particulate OM (POM) and mineral-associated OM (MAOM) are generally accepted as important functional SOM fractions, that enable the prediction of SOM dynamics (Lavalley et al., 2020). POM is mainly of plant origin, with wide C to N ratios (Gregorich et al., 2006) and predominantly consists of OM in early stages of decomposition. It can be further divided into free POM (fPOM) outside of aggregates (i.e. unprotected) and occluded POM (oPOM), the latter being physically protected from decomposition in aggregates (Six et al., 2002). C inputs, e.g. via organic fertilizers, are essential for the accumulation of OM, which positively influences soil aggregation and aggregate stability (Karami et al., 2012; Kong et al., 2005), with POM and microbially secreted substances serving as major binding agents (Costa et al., 2018; Golchin et al., 1994; Oades and Waters, 1991). All POM forms represent a dynamic, labile SOM pool that is distinctly affected by agricultural management practices (Poeplau and Don, 2013). The stability of oPOM varies widely with turnover times from years to decades depending on aggregate turnover

(Lavallee et al., 2020; Liao et al., 2006). Large aggregates have a shorter turnover time, contain younger and less decomposed SOM (Puget et al., 2000), whereas smaller aggregates are more stable and contain older and more processed SOM (Six et al., 2000; Steffens et al., 2011).

In contrast, MAOM is further decomposed, microbially transformed and stabilized through sorption onto surfaces of fine-sized mineral particles (Basile-Doelsch et al., 2015; Cotrufo et al., 2019; Kleber et al., 2015; Newcomb et al., 2017). This stabilization mechanism increases SOM turnover rates to ranges of decades up to centuries (Kleber et al., 2015; Kögel-Knabner et al., 2008b). Thus, MAOM represents a stable SOM pool, enriched with chemical components of microbial origin and low C to N ratios (Courtier-Murias et al., 2013). The extent of microbially transformed SOM from OM inputs is largely constrained by stoichiometric imbalances between OM inputs and microbial communities, i.e. elemental plant resource composition and nutrient requirements of microbial biomass (Mooshammer et al., 2014). The input of supplementary nutrients (e.g. via mineral fertilizers) might alleviate these constraints and increase the rate to which OM inputs are transferred into the stable SOM pool (Kirkby et al., 2016; Kirkby et al., 2014).

However, Steffens et al. (2009) claimed that this fraction, which is considered stable, can be mobilized and mineralized when land management and climatic conditions are changing. With advancing global warming, substantial losses of SOM from agricultural soils are projected (Wiesmeier et al., 2016), posing a challenge to efforts to increase or even maintain current soil C stocks through C inputs (Riggers et al., 2021). Given these premises, it is essential to understand how long it takes until C inputs to arable land are transferred to different functional SOM pools and for how long the sequestered C is stabilized (Schmidt et al., 2011; Smith, 2005).

The objective of this study was to investigate the temporal dynamics of quantity and quality of SOM fractions in different farming systems in the DOK long-term experiment (Therwil, CH) (Mäder et al., 2002). Our research focused on four farming systems: two conventional systems, one with the exclusive use of mineral fertilizer (CONMIN), and another with the use of mineral fertilizer and farmyard manure (CONFYM), an organic farming system with only organic manure (BIODYN) and an unfertilized control (NOFERT).

There is an extensive body of literature covering different perspectives of farming system impacts on soil properties in the DOK experiment. However, only two studies analyzed C dynamics (Fließbach et al., 2007; Leifeld et al., 2009), none of which considered the stable clay-sized MAOM fraction for testing of climate-friendly soil management. We hypothesized, that the POM fractions would reflect the continuous OM inputs, and thus farming systems receiving organic fertilizers (CONFYM and BIODYN) would accumulate significantly more labile POM than systems without organic fertilization (NOFERT and CONMIN). For the MAOM fraction, we hypothesized a steady decline towards a new steady-state

equilibrium at a lower level, where we expected the dynamics of C incorporation into this fraction to differ between the analyzed systems and to be most efficient in BIODYN and in CONFYM due to the higher microbial activity in these plots. We aimed to answer, if farming systems differing in form and amount of added fertilizers have measurable effects on functional SOM fractions, and if recommendations for climate-friendly soil management can be drawn from long-term experiments.

2.2. Materials and Methods

2.2.1. Experimental setup and sampling

The DOK field experiment is a long-term farming system comparison trial, located in Therwil, Canton of Basel Landschaft, Switzerland (7°32' E, 47°30' N), which started in 1978. The soil type is a Haplic Luvisol (WRB, 2015), developed on deep deposits of alluvial loess. The mean annual temperature is 10.5 °C (1.5 °C increase since 1978) with a mean annual precipitation of 840 mm (Krause et al., 2020). In the DOK trial, two organic and two conventional farming systems are compared with an unfertilized control (Mäder et al., 2002). They have the same crop rotation within seven-year crop rotation periods (CRP) with two years of grass-clover ley (**Table S2.1**), but receive different types of fertilizers. Each farming system is replicated four times (columns), and the crop rotation is running temporally shifted in three subplots. This sums up to 96 parcels (5 × 20 m each), arranged in a randomized split-plot design. All farming systems have the same type and frequency of tillage but receive different types of plant protection (**Table 2.1**).

The focus of this study was on four systems, which represent an input gradient of fertilizers in terms of quantity and quality of OM input (**Table 2.1**). NOFERT (NO FERTilization) is a control treatment that has received no fertilizers since 1978. CONMIN (CONventionally managed and MINeral fertilizer) receives only mineral fertilizer and was left unfertilized during the first CRP (1978-1984). CONFYM (CONventionally managed, mineral fertilizer and FarmYard Manure) is an integrated conventional system, that combines the use of mineral and organic fertilizers, and BIODYN (BIODYNamicallly managed) receives only organic fertilizers (**Table 2.1**), and is managed according to principles of biodynamic farming. Straw biomass was removed from the plots after harvesting. In CONFYM and BIODYN, manure amendment corresponds to 1.4 livestock units per hectare and year (**Table 2.1**). The amount of raw manure prior to farming system-specific processing, defines the amount of OM inputs via organic fertilizers in CONFYM and BIODYN. Aerobic composting of BIODYN manure results in higher C losses via microbial decomposition, compared to manure stacking in CONFYM, manifested by 20% lower OM inputs in BIODYN (**Table 2.1**). Qualitatively, BIODYN compost is relatively enriched with more recalcitrant OM due to the higher losses of labile C compounds (Fließbach and Mäder, 2000). Slurry is added to supply nutrients according to plant needs, mainly N, of the given crop. Mineral nutrient inputs in CONMIN and CONFYM are given up to the limits of Swiss fertilization recommendations (Richner and Sinaj, 2017). Mineral fertilizers were added on top of manure in CONFYM to reach the recommended N level, and as N inputs from farmyard manure are not fully accounted for as readily bioavailable, CONFYM received higher N inputs than CONMIN (**Table 2.1** & **Table S2.2**).

Overall, we analyzed archived soil samples from 16 plots (four farming systems with four replicates each) taken every fifth year (1982, 1989, 1996, 2003, 2010 and 2017) within each of the six completed seven-year CRP (CRP 1 = 1978-1984, CRP 2 = 1985-1991, CRP 3 = 1992-1998, CRP 4 = 1999-2005, CRP 5 = 2006-2012, CRP 6 = 2013-2019) (**Table S2.1**). This resulted in 96 bulk soil samples in total, each representing a composite of 15-20 randomly distributed samples, taken after harvest with a soil corer (0-20 cm depth, 3 cm diameter) in the inner part of the plots, leaving out border zones. Samples were transported to the lab, air-dried at 40 °C, until no further moisture loss was observed and subsequently sieved to 2 mm.

2.2.2. Soil characterization

We analyzed all 16 plots for their basic soil characteristics, to provide an assessment of the current state of the studied soils. Therefore, bulk SOC and total N were measured on the most recent archived samples from 2017, while texture and mineralogy were analyzed using the most recent soil samples from the latest DOK sampling campaign in 2019 (**Table 2.2**).

2.2.2.1. Bulk SOC and total N

Bulk SOC and total N content were determined in duplicate via dry combustion on a Vario EL cube elemental analyzer (Elementar Analysensysteme, Hanau, Germany). All bulk samples were free of carbonates so that the total C concentration equals the organic C (OC) concentration.

2.2.2.2. Texture

The texture of bulk soil samples was determined with the PARIO Plus Soil Particle Analyzer (METER Group, Germany/USA). Prior to measurement, H₂O₂ (30%) was added to 25-30 g of soil sample and heated in a water bath for OM oxidation (12 h). H₂O₂ was removed from the sample through subsequent repeated addition of distilled water, centrifuging and decanting. We repeatedly washed the samples until an electrical conductivity of <400 $\mu\text{S m}^{-1}$ was reached, to ensure the absence of soluble salts. Sodium hexametaphosphate (Na₆O₁₈P₆) was used for sample dispersion.

2.2.2.3. Mineralogy

Mineralogy of the bulk soil and the clay fraction (<2 μm and <6.3 μm) was determined using powder X-ray diffraction (P-XRD, Cubix³, Malvern Panalytical, Almelo, Netherlands). Prior to P-XRD analyses, the samples were treated with hydrogen chloride (HCl) to remove OM. P-XRD was performed on random powder samples and on oriented samples after saturation with Ca²⁺ and ethylene glycol (room temperature) and K⁺ (room temperature and stepwise heated to 550 °C).

Table 2.1: Overview of the four farming systems, their respective types of fertilization, pest and weed control, and average annual organic matter (OM) inputs via organic fertilizers between 1982 and 2017 in the analyzed subplot in the DOK system comparison trial. Modified from Krause et al. (2020). In CONFYM and BIODYN, the addition of organic fertilizer is equivalent to the manure and slurry produced by 1.4 LU (livestock units fertilization equivalents) $\text{ha}^{-1} \text{yr}^{-1}$. 1 LU approximately corresponds to 105 kg N, 15 kg P and 149 kg K (Richner and Sinaj, 2017).

farming system	LU [$\text{ha}^{-1} \text{yr}^{-1}$]	fertilizer	OM inputs via manure and slurry (1982-2017) [$\text{kg ha}^{-1} \text{yr}^{-1}$]	weed control	disease control	pest control	special treatments
NOFERT (control)	-	-	-	mechanical	indirect	biocontrol	-
CONMIN (conventional)	-	mineral N, P, K	-	mechanical, herbicides	fungicides (thresholds)	insecticides (thresholds)	plant growth regulators
CONFYM (conventional)	1.4	mineral N, P, K, stacked manure and slurry	2508	mechanical, herbicides	fungicides (thresholds)	insecticides (thresholds)	plant growth regulators
BIODYN (organic)	1.4	biodynamic composted manure and slurry	2000	mechanical	indirect	plant extracts, biocontrol	biodynamic preparations

Table 2.2: Bulk soil characteristics (<2000 μm , 0-20 cm depth) of all 16 observed plots. Texture and mineralogy were analyzed with soil samples from 2019. C and N analyses were conducted with soil samples from 2017. Arithmetic means of farming systems are depicted with standard deviations. Significant differences between systems at $p < 0.05$ are indicated by post-hoc Tukey letters.

farming system	plot	Texture			Main mineralogy						Clay mineralogy						C/N
		Sand (2000-63 μm) [%]	Silt (63-2 μm) [%]	Clay (<2 μm) [%]	Quartz [%]	Feldspars [%]	Fe oxides/hydroxides [%]	Carbonates [%]	Phyllosilicates [%]	Illite [%]	Smectite [%]	Chlorite [%]	Kaolinite [%]	OC [mg g^{-1}]	N_{tot} [mg g^{-1}]		
NOFERT	3	3.0	77.6	19.5	58.4	17.7	2.0	0.4	21.6	11.7	4.6	4.3	1.0	12.8	1.5	8.5	
	37	3.1	81.5	15.5	61.1	18.8	1.5	0.7	18.0	10.9	2.7	3.5	0.9	10.1	1.2	8.3	
	59	3.0	75.8	21.1	59.5	19.4	1.6	1.0	18.6	11.3	2.7	4.5	0.1	10.2	1.2	8.3	
	93	1.8	73.5	24.8	56.8	18.1	2.1	1.3	21.7	8.6	7.3	2.7	3.0	12.2	1.5	8.3	
	\bar{x}	2.7 \pm 0.6	77.1 \pm 3.4	20.2 \pm 3.9	59.0 \pm 1.8	18.5 \pm 0.8	1.8 \pm 0.3	0.9 \pm 0.4	20.0 \pm 2.0	10.6 \pm 1.4	4.3 \pm 2.2	3.8 \pm 0.8	1.3 \pm 1.2	11.3 \pm 1.4	1.4 \pm 0.2	8.4 \pm 0.1	
CONMIN	4	2.9	75.2	21.9	60.1	16.8	1.7	0.6	20.8	12.9	3.1	2.9	1.9	14.4	1.6	8.8	
	38	3.2	76.2	20.7	58.3	20.4	1.7	0.2	19.4	10.9	4.2	2.0	2.3	12.0	1.4	8.7	
	60	2.7	77.4	19.9	62.5	19.3	1.8	0.7	15.7	8.0	4.1	1.8	1.9	12.5	1.5	8.6	
	94	2.3	73.5	24.3	53.0	17.7	2.4	0.6	26.3	16.9	3.9	4.3	1.3	15.3	1.8	8.6	
	\bar{x}	2.8 \pm 0.4	75.6 \pm 1.7	21.7 \pm 1.9	58.5 \pm 4.0	18.6 \pm 1.6	1.9 \pm 0.3	0.5 \pm 0.2	20.6 \pm 4.4	12.2 \pm 3.7	3.8 \pm 0.5	2.8 \pm 1.1	1.9 \pm 0.4	13.6 \pm 1.6	1.6 \pm 0.2	8.7 \pm 0.1	
CONFYM	22	2.5	76.1	21.4	59.5	21.2	1.3	0.6	17.5	11.4	2.5	3.2	0.4	13.8	1.6	8.5	
	32	3.1	80.4	16.5	58.2	18.6	1.6	0.6	21.0	14.7	2.6	3.1	0.6	16.3	1.8	8.9	
	66	2.4	75.2	22.4	59.6	17.6	1.7	0.7	20.4	14.1	2.4	3.7	0.3	14.5	1.7	8.6	
	76	3.4	75.4	21.2	56.2	20.1	1.7	0.6	21.5	14.4	2.6	3.4	1.1	13.9	1.6	8.8	
	\bar{x}	2.9 \pm 0.5	76.8 \pm 2.4	20.4 \pm 2.6	58.4 \pm 1.6	19.4 \pm 1.6	1.6 \pm 0.2	0.6 \pm 0.1	20.1 \pm 1.8	13.7 \pm 1.5	2.5 \pm 0.1	3.4 \pm 0.3	0.6 \pm 0.4	14.6 \pm 1.2	1.7 \pm 0.1	8.7 \pm 0.2	
BIODYN	10	3.4	74.9	21.7	56.3	16.7	1.9	0.5	24.7	12.1	7.6	2.4	2.6	18.5	2.0	9.1	
	44	2.2	76.2	21.7	59.5	20.7	1.6	0.7	17.5	11.5	2.1	2.0	1.9	17.0	1.9	9.0	
	54	3.8	74.9	21.3	63.2	17.5	1.7	0.7	16.9	11.5	1.8	2.2	1.4	15.0	1.8	8.7	
	88	1.5	69.2	29.3	49.7	16.3	1.6	0.9	31.5	21.0	4.2	2.6	3.7	21.0	2.4	8.7	
	\bar{x}	2.7 \pm 1.1	73.8 \pm 3.1	23.5 \pm 3.9	57.2 \pm 5.7	17.8 \pm 2.0	1.7 \pm 0.1	0.7 \pm 0.2	22.7 \pm 6.9	14.0 \pm 4.7	3.9 \pm 2.7	2.3 \pm 0.3	2.4 \pm 1.0	17.9 \pm 2.5	2.0 \pm 0.3	8.9 \pm 0.2	

2.2.3. Physical fractionation

Following a modified fractionation scheme of Kölbl and Kögel-Knabner (2004) and Steffens et al. (2009), we separated POM and MAOM fractions from all 96 bulk soil samples (**Figure 2.1**) (for the detailed laboratory method see **S1.1**). Briefly, 250 ml of Na-polytungstate solution ($\rho = 1.8 \text{ g cm}^{-3}$; TC-Tungsten Compounds, Grub am Forst, Germany) was added to 30 g of air-dried bulk soil ($<2 \text{ mm}$) for capillary saturation and left settling overnight. The floating fPOM was aspirated with a vacuum pump. Using ultrasound for aggregate disruption, subsequent centrifugation and aspiration, the further decomposed POM, receiving physical protection through occlusion (oPOM) within macro-aggregates of the heavy fraction ($>1.8 \text{ g cm}^{-3}$) was separated.

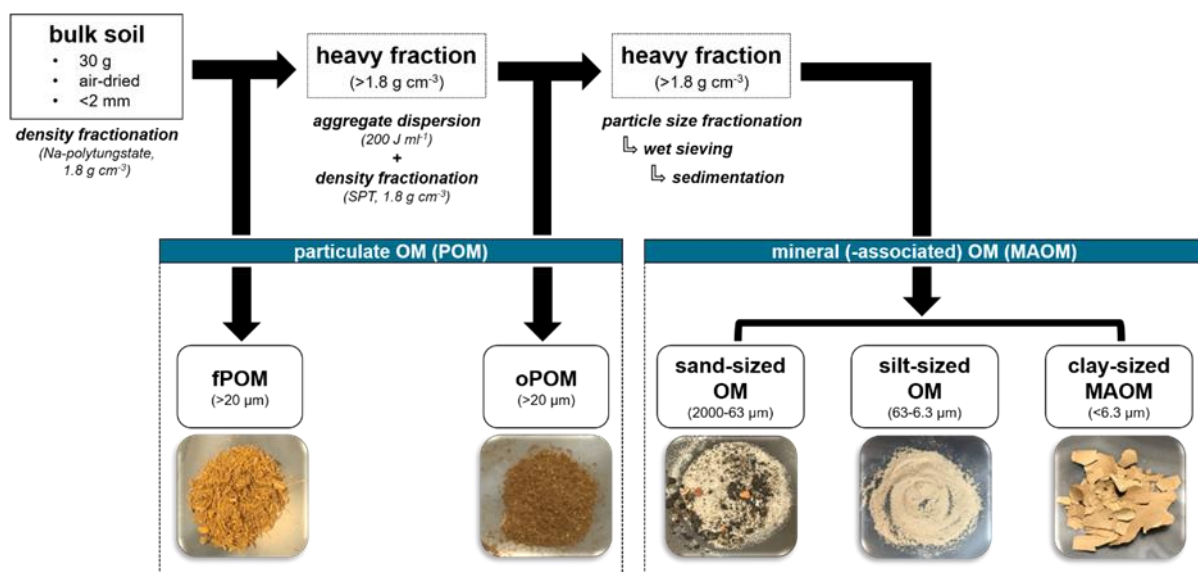


Figure 2.1: Physical fractionation scheme and conducted measurements. Modified from Kölbl and Kögel-Knabner (2004) and Steffens et al. (2009). The coarse silt ($63\text{--}20 \mu\text{m}$) and medium silt fraction ($20\text{--}6.3 \mu\text{m}$) were put together and referred to as silt-sized OM ($63\text{--}6.3 \mu\text{m}$), and the fine silt + clay fraction is referred to as clay-sized MAOM fraction ($<6.3 \mu\text{m}$).

Prior, we tested a range of ultrasonic energies ($50\text{--}450 \text{ J ml}^{-1}$) (**Figure S1.1**) for optimal aggregate disruption, adjusted to the texture and C content of the samples (Griepentrog and Schmidt, 2013). 200 J ml^{-1} released the most oPOM-C and therefore disrupted macro-aggregates most efficiently, minimizing redistribution of POM into finer particle-size fractions (Oorts et al., 2005). The ultrasonic homogenizer (Sonopuls HD 2200.2, Bandelin, Berlin, Germany) operated at a constant output of 75 W. A calorimetric calibration (North, 1976) of the ultrasonic device was regularly conducted, due to considerable deviations between nominal and actual energy outputs of ultrasonifiers (Schmidt et al., 1999), caused by deterioration of the probe tip (Amelung and Zech, 1999; Mentler et al., 2017). The probe tip of the sonotrode (VS 70 T, 13 mm diameter, Bandelin, Berlin, Germany) was immersed 25 mm into the solution for complete turbation of the sample. We regulated the temperature of the solution ($<30 \text{ }^\circ\text{C}$) to prevent alteration of SOM quality. The obtained POM fractions were washed ($<10 \mu\text{S cm}^{-1}$)

over a 20 μm sieve, freeze-dried, weighed and ground for further analyses. The remaining heavy fraction ($> 1.8 \text{ g cm}^{-3}$) was washed ($< 50 \mu\text{S cm}^{-1}$) via centrifugation (15 min, 7000 rpm) and wet-sieved to separate the sand (2000-63 μm) and the coarse silt fraction (63-20 μm).

Prior to further fractionation by sedimentation in Atterberg-cylinders, we conducted tests to choose between a particle size cut-off at $< 2 \mu\text{m}$ or $< 6.3 \mu\text{m}$. Both fractions were separated from four replicates of one NOFERT and of one BIODYN plot, and ^{14}C age was determined (Mini Carbon Dating System, MICADAS, ETH Zürich, Switzerland). We found no significant differences between ^{14}C ages of the two fractions in neither of the two farming systems (data not shown). Thus we used a particle size cut-off at $< 6.3 \mu\text{m}$, because of the considerable increase in material and the reduction of sedimentation time. This fraction is denominated as clay-sized MAOM fraction ($< 6.3 \mu\text{m}$).

Eventually, fPOM ($> 20 \mu\text{m}$), oPOM ($> 20 \mu\text{m}$), sand-sized OM (2000-63 μm), silt-sized OM (63-6.3 μm) and clay-sized MAOM ($< 6.3 \mu\text{m}$) were separated. OM in the sand- and silt-sized fractions is probably not adsorbed to surfaces of these mineral particles, but rather originates as methodological artifact from fractionation procedures (e.g. wet-sieving) and still intact micro-aggregates (after ultrasonication). This is why only the clay-sized fraction ($< 6.3 \mu\text{m}$) was assigned the term 'MAOM'. All obtained fractions were air-dried at 60 $^{\circ}\text{C}$, weighed and ground for further analyses.

2.2.4. OC, total N, and calculation of mass and C recovery

We analyzed all archived bulk soil samples ($n = 16 \text{ plots} \times 6 \text{ years} = 96$) and obtained SOM fractions from physical fractionation ($n = 96 \text{ bulk soil samples} \times 5 \text{ fractions} = 480$) in duplicate for total C and N concentrations by dry combustion on a Vario EL cube elemental analyzer (Elementar Analysensysteme, Hanau, Germany). All bulk samples were free of carbonates so that the total C concentration equals the organic C (OC) concentration. The sum of the weights of all separated and air-dried fractions ($n = 5$) per bulk soil sample (30 g) gave the corresponding mass recovery. Measured OC concentration of each fraction was applied against the respective fraction weights, and the sum of all five fractions compared to the measured OC concentration of the bulk soil gave the C recovery.

In addition, we calculated the maximum potential C saturation of mineral particles $< 20 \mu\text{m}$ according to the empirical formula of Hassink (1997) and its adjustments made by Wiesmeier et al. (2015) to consider texture differences between the analyzed plots:

$$C_{pot} = a + b * particles_{<20\mu\text{m}}$$

C_{pot} is the maximum potential C saturation of mineral particles $< 20 \mu\text{m}$ [mg g^{-1}], a and b are empirically determined constants ($a_{\text{Hassink}} = 4.09$ and $b_{\text{Hassink}} = 0.37$; $a_{\text{Wiesmeier}} = -0.23$ and $b_{\text{Wiesmeier}} = 0.36$).

$particles_{<20\mu m}$ is the concentration of mineral particles $<20 \mu m$ [%], determined by texture analysis. Further, we calculated the current C contents (C_{cur}) [$mg g^{-1}$] of this fraction for 1982 and 2017, using its measured OC concentrations and fraction mass proportions determined by texture analysis. C saturation (C_{sat}) is the percentage of C_{cur} from C_{pot} , and the C saturation deficit (C_{def}) is calculated as $C_{pot} - C_{cur}$.

2.2.5. Solid-state ^{13}C CPMAS-NMR spectroscopy

Selected fPOM ($n = 2-3$ plot replicates per farming system), oPOM ($n = 2-4$ plot replicates per farming system) and clay-sized MAOM fractions ($n = 4$ NOFERT and 4 BIODYN plot replicates) from 1982 and 2017 were analyzed by solid-state ^{13}C cross-polarization magic-angle spinning nuclear magnetic resonance (CPMAS-NMR) spectroscopy (Bruker DSX 200 NMR spectrometer, Bruker, Karlsruhe, Germany), to determine the OM chemical compositions. Clay-sized MAOM fractions were treated with hydrofluoric acid (HF) prior to measurement, to reduce mineral particle contents and enrich ^{13}C . We conducted measurements in 7 mm zirconium dioxide rotors at a spinning speed of 6800 Hz and a pulse delay time of 0.4 s. A ramped 1H pulse was applied during a contact time of 1 ms, to avoid Hartmann-Hahn mismatches. Depending on the C contents and available sample material, the number of obtained scans ranged between 3'600 and 205'000, and a line broadening between 0 and 100 Hz was applied for the spectra. The ^{13}C chemical shifts were referenced to tetramethylsilane (0 ppm). We used the following chemical shift regions for integration: -10 to 45 ppm (alkyl C), 45 to 110 ppm (O/N alkyl C), 110 to 160 ppm (aromatic C) and 160 to 220 ppm (carbonyl/carboxyl C). The ratio of alkyl C to O/N alkyl C (A/O-A ratio) was used as sensitive indicator for the degree of OM decomposition (Baldock et al., 1997).

2.2.6. Statistical analyses

We applied a linear mixed effects model with repeated measurements to determine the impact of farming systems on SOM fractions as a function of sampling year, using R version 4.1.2 and RStudio (RStudio Team, 2021). In short, the lme function of the nlme package was used (Pinheiro et al., 2020) with farming system nested in subplot and column as repeated random factors to account for spatial heterogeneity within the experimental design of the DOK trial. A two-way ANOVA was then employed to determine the impact of farming system, sampling year and their interaction on SOC contents. Subsequently, a Tukey HSD test was applied to test for differences between the farming systems, in case of model significance. Differences in bulk soil characteristics and chemical shift regions of obtained ^{13}C CPMAS-NMR spectra between the farming systems were tested for statistical significance by a one-way ANOVA. Residuals were tested for normal distribution using visual inspection of QQ-plots and the Shapiro-Wilk test, and homogeneity of variances was tested using Levene's test. Subsequently, a post-hoc Tukey HSD test was performed using a significance level of $\alpha = 0.05$, for all tests.

2.3. Results

2.3.1. Bulk soil characteristics

All analyzed plots had a silty texture with $2.8 \pm 0.6\%$ sand, $75.8 \pm 2.8\%$ silt and $21.4 \pm 3.2\%$ clay (**Table 2.2**). Mean sand (NOFERT: $2.7 \pm 0.6\%$, CONMIN: $2.8 \pm 0.4\%$, CONFYM: $2.9 \pm 0.5\%$ and BIODYN: $2.7 \pm 1.1\%$), silt (NOFERT: $77.1 \pm 3.4\%$, CONMIN: $75.6 \pm 1.7\%$, CONFYM: $76.8 \pm 2.4\%$ and BIODYN: $73.8 \pm 3.1\%$) and clay contents (NOFERT: $20.2 \pm 3.9\%$, CONMIN: $21.7 \pm 1.9\%$, CONFYM: $20.4 \pm 2.6\%$ and BIODYN: $23.5 \pm 3.9\%$) showed comparable values between the plots of the farming systems after harvest in 2019. All 16 plots showed similar mineralogies, with phyllosilicate contents around 20%, dominated by illite, which was lowest under NOFERT ($10.6 \pm 1.4\%$) and highest under BIODYN ($14.0 \pm 4.7\%$) (**Table 2.2**). Mean SOC contents in 2017 were lowest in NOFERT ($11.3 \pm 1.4 \text{ mg g}^{-1}$), higher in CONMIN ($13.6 \pm 1.6 \text{ mg g}^{-1}$) and CONFYM ($14.6 \pm 1.2 \text{ mg g}^{-1}$), and highest in BIODYN ($17.9 \pm 2.5 \text{ mg g}^{-1}$) (**Table 2.2**), with significant differences to CONMIN and NOFERT (**Figure 2.2**).

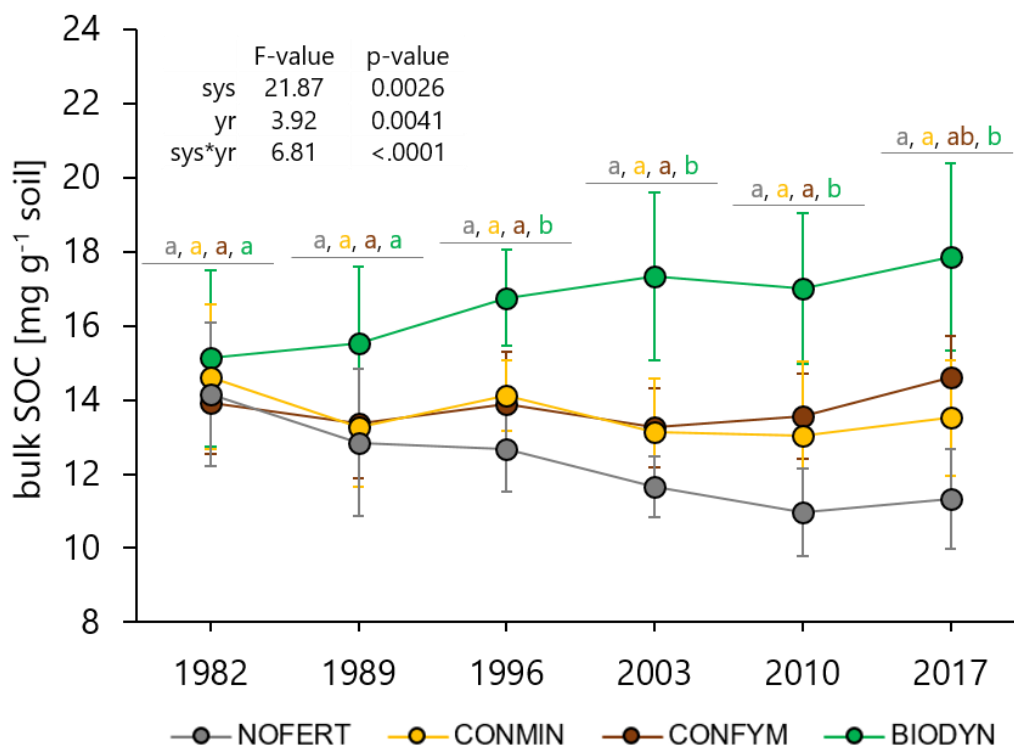


Figure 2.2: Development of bulk SOC contents in the DOK trial (0–20 cm depth) under each farming system over a 36-year period (1982–2017). Data shows plot means ($n = 4$) per farming system and year. Error bars represent standard deviations between the four replicated plots per farming system. Results of a repeated two-way ANOVA ($sys =$ farming system, $yr =$ year) are depicted, using a linear mixed effect model that accounts for the spatial arrangement of plots within the experimental design. Post-hoc Tukey letters give significant differences at $p < 0.05$.

2.3.2. Physical fractionation

2.3.2.1. Bulk SOC development

Bulk SOC contents in the four different farming systems developed as follows from 1982 to 2017: in NOFERT, it decreased by 2.8 mg g^{-1} (-20%) and in CONMIN by 1.1 mg g^{-1} (-8%). In CONFYM, it slightly increased by 0.7 mg g^{-1} (+5%) and in BIODYN by 2.7 mg g^{-1} (+13%) (**Figure 2.2**).

2.3.2.2. Distribution and development of C in POM and MAOM fractions

The averaged mass recovery over all farming systems and years after physical fractionation was $94 \pm 1\%$, and SOC recovery averaged $73 \pm 4\%$. Both recovery rates showed similar values between farming systems and years. Based on these recovery rates, on average 8.0% of SOC was stored in POM fractions ($>20 \mu\text{m}$) (3.3% fPOM, 4.7% oPOM), 1.8% in the sand-sized OM fraction (2000-63 μm), 20.8% in the silt-sized OM fraction (63-6.3 μm) and 69.4% in the clay-sized MAOM fraction ($<6.3 \mu\text{m}$). The absolute values of fraction-C contents per farming system for each analyzed year are presented in **Table S2.3**.

C contents in the fPOM fraction were relatively stable over the whole period with minor increases in all treatments (**Figure 2.3a**). Depending on farming system, oPOM-C contents showed major fluctuations. In NOFERT and CONMIN, they were relatively stable from 1982 to 2010. In 2017, oPOM-C increased in these systems by +161% and +87%, respectively, compared to 2010. In CONFYM and BIODYN, the development of oPOM-C contents was characterized by strong fluctuations between the analyzed years (**Figure 2.3b**). From 1982 to 1989, oPOM-C in CONFYM and BIODYN increased by 106% and 145%, followed by a decrease of 66% and 50% from 1989 to 1996, respectively. The same but attenuated pattern was observed from 1996 to 2003, with oPOM-C increases of 56% and 70% and decreases of 58% and 48% from 2003 to 2010, respectively. In 2017, oPOM-C contents recorded their biggest increases of 289% in CONFYM and 184% in BIODYN. We found these oPOM-C fluctuations to strongly correlate with the elapsed time between harvest and sampling (R^2 ; BIODYN: 0.87; CONFYM: 0.96) each analyzed year, which ranged from 1 to 35 days (**Figure 2.4**).

The sand-sized OM (2000-63 μm) fraction contributed the least to the total SOC content and slight fluctuations between the sampled years are assumed to be artefacts of methodical issues during fractionation, specifically wet-sieving. Therefore, the share of SOC in this fraction is rather negligible. In the silt-sized OM (63-6.3 μm) fraction, SOC contents decreased in all treatments from 1982 to 2017. In NOFERT 24%, in CONMIN 9%, in CONFYM 5% and in BIODYN 5% of SOC were lost (**Figure 2.5a**).

From 1982 to 2017, SOC contents in the clay-sized MAOM ($<6.3 \mu\text{m}$) fraction decreased in NOFERT (-27%) and CONMIN (-14%), while in CONFYM (-3%) and in BIODYN ($\pm 0\%$) they remained stable (**Figure 2.5b**). Between BIODYN and NOFERT, significant differences in clay-sized MAOM-C contents were

detected from 2003 until 2017. CONFYM and CONMIN had similar SOC contents in the clay-sized MAOM fraction throughout the whole observation period and showed no significant differences to either NOFERT or BIODYN.

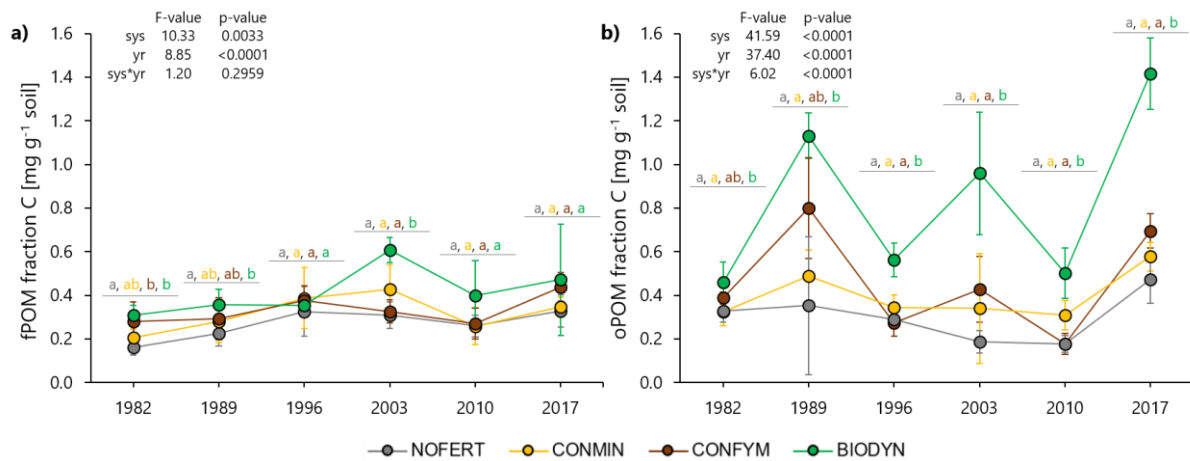


Figure 2.3: Development of mean SOC contents in **a)** the fPOM (>20 μm) and **b)** the oPOM (>20 μm) fraction from 1982 to 2017 in all farming systems. Error bars represent standard deviations between the replicated plots (n = 4) per farming system. Results of a repeated two-way ANOVA (sys = farming system, yr = year) are depicted, using a linear mixed effect model that accounts for the spatial arrangement of plots within the experimental design. Post-hoc Tukey letters give significant differences at p < 0.05.

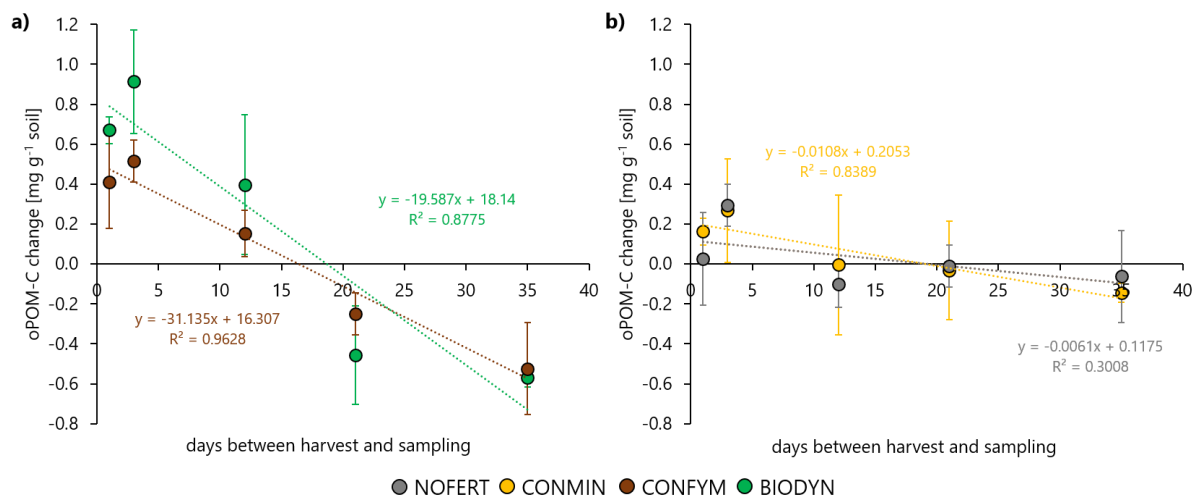


Figure 2.4: Correlation of oPOM-C changes and days between harvest and sampling under **a)** organically fertilized management (BIODYN and CONFYM) and **b)** under exclusion of organic fertilizers (CONMIN and NOFERT). Error bars represent standard deviations between the replicated plots (n = 4) per farming system.

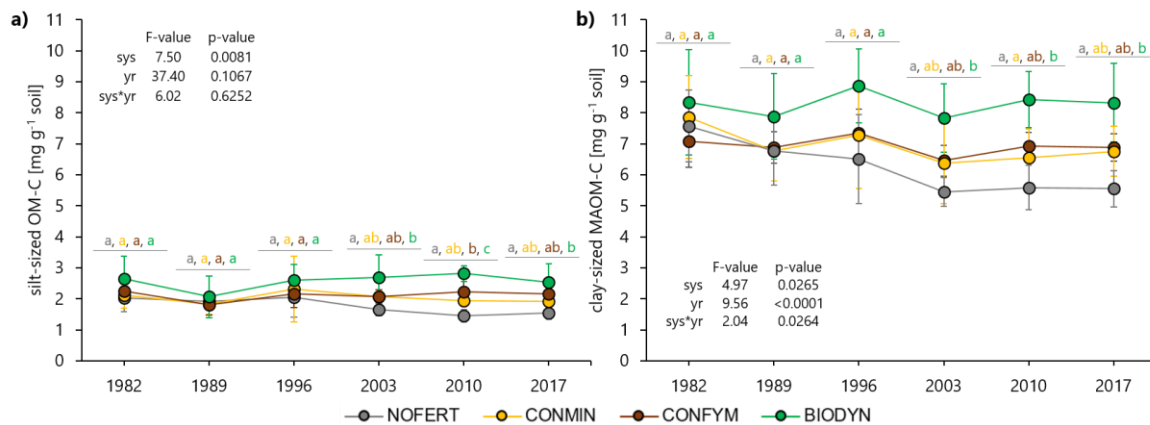


Figure 2.5: Development of SOC contents in **a)** the silt-sized OM fraction (63–6.3 μm) and **b)** in the clay-sized MAOM fraction (<6.3 μm) from 1982 to 2017. Error bars represent standard deviations between the replicated plots ($n = 4$) per farming system. Results of a repeated two-way ANOVA (sys = farming system, yr = year) are depicted, using a linear mixed effect model that accounts for the spatial arrangement of plots within the experimental design. Post-hoc Tukey letters give significant differences at $p < 0.05$.

The potential C saturation (C_{pot}) of the fine fraction (<20 μm), across all analyzed systems averaged 25.0 and 20.1 mg g^{-1} , according to the empirical formulas of Hassink (1997) and Wiesmeier et al. (2015) (**Table S2.4**). C saturation (C_{sat}) of the fine fraction across all systems averaged 52.1% and 64.7% in 1982, and was lowest in NOFERT (Hassink: 49.4%, Wiesmeier: 61.5%) and highest in BIODYN (Hassink: 55.0%, Wiesmeier: 67.8%) (**Figure 2.6a**). In 2017, C_{sat} decreased in all systems, but remained the same in BIODYN (Hassink: 53.9%, Wiesmeier: 66.6%) (**Figure 2.6b**). Concomitantly, C saturation deficits (C_{def}) increased in all systems from 1982 to 2017, but stayed the same in BIODYN.

In addition, the SOC to clay (SOC:clay) ratio, as an indicator for soil structural quality (Johannes et al., 2017), was <1:10 for all studied plots over the observed period from 1982 to 2017 (**Figure 2.6c & 2.6d**). Averaged over all systems, we observed a linear correlation between 2:1 phyllosilicates (i.e. illite and smectite) and C contents in the clay-sized MAOM fraction (<6.3 μm) in all analyzed plots (1982: $R^2 = 0.6493$, 2017: $R^2 = 0.5002$) (**Figure 2.7**).

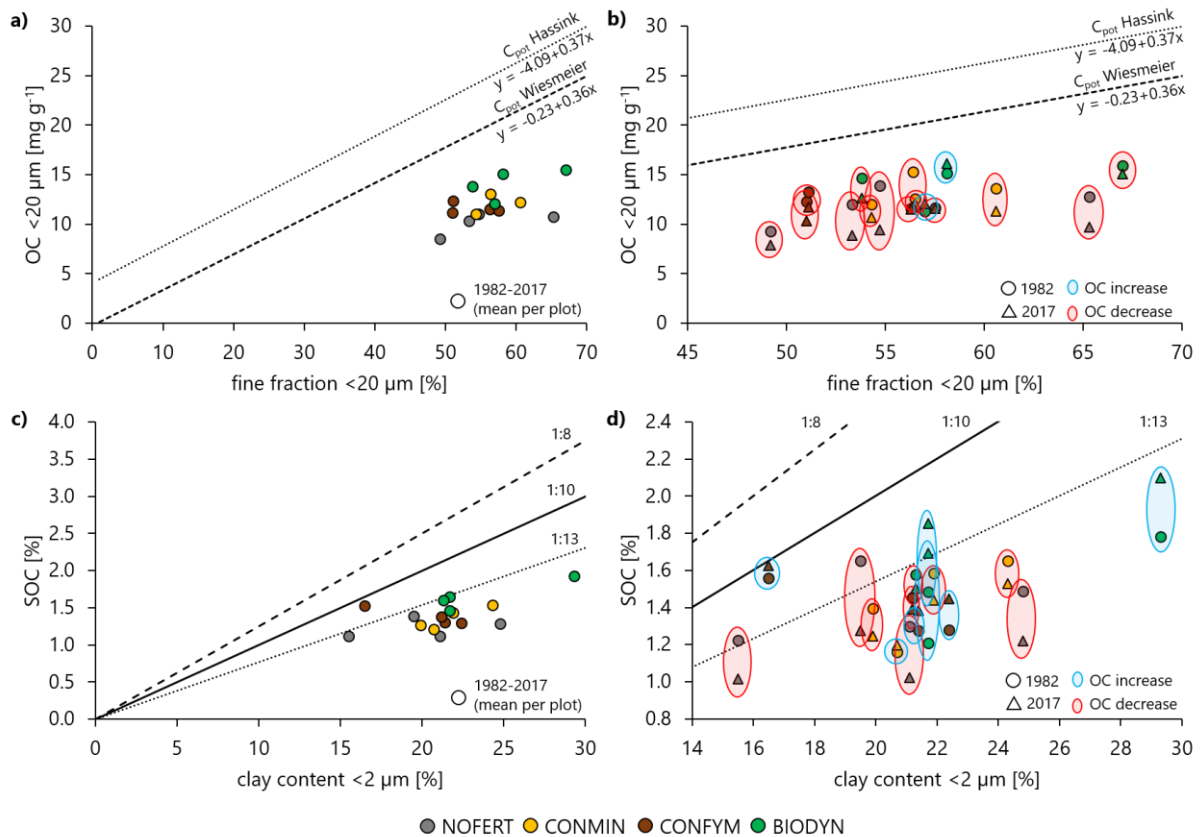


Figure 2.6: Correlations of fine fraction (<20 μm) OC concentration with its mass proportion (i.e. C saturation, C_{sat}) compared to linear regressions according to Hassink (1997) and Wiesmeier et al. (2015) (C_{pot}) (upper two graphs). Correlations of clay content (<2 μm ; %) with SOC (%) according to Johannes et al. (2017) (lower two graphs). The dashed, solid and dotted lines depict a SOC:clay ratio of 1:8, 1:10 and 1:13, respectively. A SOC:clay ratio of 1:10 is seen as reasonable goal for soil management, as its decrease leads to a lower soil structural quality. Overall, values are calculated with PARIO texture (2019) and C concentrations from elemental analysis for **a**) and **c**) each analyzed plot averaged over the observation period, and **b**) and **d**) "zoomed in" to follow the development per plot from the first (1982) to the last year of analysis (2017).

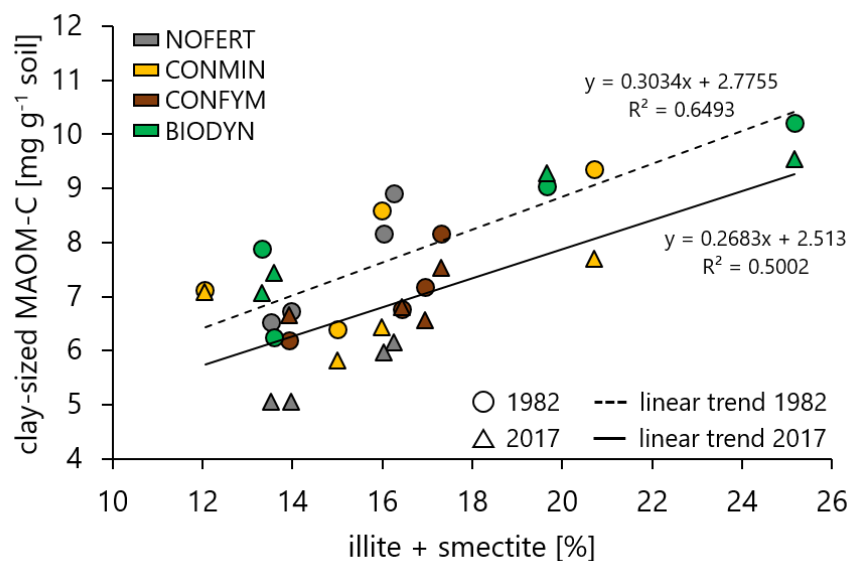


Figure 2.7: Linear correlation between 2:1 phyllosilicates (i.e. illite and smectite) (%) as measured with XRD analysis on soil samples from 2019, and C contents in the clay-sized MAOM fraction (<6.3 μm) (mg g^{-1} soil) in all 16 analyzed plots. Circles depict values from 1982 and triangles from 2017. The dashed and solid lines represent the linear trends in 1982 and 2017, respectively.

2.3.2.3. Chemical composition of POM and MAOM fractions

Across all analyzed fractions, systems and years, NMR spectra were dominated by alkyl C and O/N-alkyl C ($67.7 \pm 2.4\%$) (**Figure S2.1 & Table 2.3**). POM fractions showed lower shares of carboxyl C ($8.86 \pm 0.9\%$) and alkyl C ($15.2 \pm 1.9\%$) and higher shares of O/N-alkyl C ($52.5 \pm 2.8\%$) compared to the clay-sized MAOM fractions (carboxyl C: $13.26 \pm 0.6\%$; alkyl C: $25.8 \pm 1.0\%$; O/N-alkyl C: $42.0 \pm 2.2\%$). This was reflected in the alkyl C to O/N-alkyl C ratios (A/O-A ratio; Baldock et al. (1997)), which increased in the order fPOM (0.27) < oPOM (0.31) < clay-sized MAOM (0.61). Within the four different systems, fPOM A/O-A ratios were highest in BIODYN (0.28) compared to the other systems (0.23) in 2017. Other than that, no considerable differences regarding chemical composition of POM fractions were found between the systems. A/O-A ratios of NOFERT and BIODYN clay-sized MAOM fractions were the same in 1982 (0.65). In 2017 however, it strongly decreased to 0.55 in NOFERT, but remained constant in BIODYN (0.62).

Table 2.3: Integrated chemical shift regions of obtained ¹³C CPMAS-NMR spectra of selected POM and MAOM fractions. Values are given as arithmetic means in bold with standard deviations of plot replicates, for POMs (n = 2-4) and clay-sized MAOM fractions (n = 4) (<6.3 μm), for 1982 and 2017. Post-hoc Tukey letters give significant differences between farming systems at p < 0.05, for > 3 plot replicates.

	Alkyl C		O/N-Alkyl C		Aryl C		Carboxyl C		Alkyl / O/N-alkyl ratio	
	1982	2017	1982	2017	1982	2017	1982	2017	1982	2017
NOFERT	26.65±0.89 a	25.02±0.99 a	40.93±0.63 a	45.34±1.73 a	18.56±0.41 a	17.08±0.19 a	13.84±0.13 a	12.55±1.05 a	0.65±0.03 a	0.55±0.04 a
BIODYN	26.59±0.82 a	24.87±1.36 a	41.20±1.12 a	40.67±3.02 a	19.10±1.37 a	20.80±1.94 b	13.08±1.22 a	13.58±0.82 a	0.65±0.03 a	0.62±0.08 a
					oPOM (> 20 μm) [%]					
NOFERT	13.92±1.33	16.96±1.27	50.86±1.69	53.40±0.68	25.79±1.32	21.37±1.11	8.71±1.79	8.06±0.71	0.27±0.02	0.32±0.03
CONMIN	17.14±1.95	14.67±0.73	47.47±3.64	53.41±1.10	24.20±3.66	23.17±1.05	10.74±1.78	8.69±1.19	0.36±0.01	0.27±0.01
CONFYM	16.62±1.62	15.29±1.22	51.03±0.61	54.66±0.35	23.55±1.80	21.97±0.98	9.07±0.06	7.98±0.48	0.33±0.03	0.28±0.02
BIODYN	17.59±1.37	17.00±0.80	50.23±0.44	51.18±2.88	22.76±1.00	22.61±2.01	9.03±1.06	8.98±1.80	0.35±0.02	0.33±0.01
					fPOM (> 20 μm) [%]					
NOFERT	11.50±3.26	13.44±0.19	50.06±5.75	57.44±7.11	28.04±2.59	20.54±4.13	9.59±0.39	8.15±2.22	0.23±0.09	0.24±0.03
CONMIN	17.86±5.25	12.85±0.78	52.13±2.70	55.76±4.98	20.61±2.51	23.25±4.18	9.79±4.67	7.96±1.13	0.34±0.08	0.23±0.01
CONFYM	14.72±0.81	12.67±1.91	55.00±5.27	55.88±4.89	22.70±4.73	22.72±3.55	7.47±0.40	8.84±3.26	0.27±0.04	0.23±0.01
BIODYN	15.81±0.13	14.80±4.29	48.75±3.48	52.46±0.49	24.90±2.19	24.05±0.75	10.32±0.53	8.39±2.65	0.33±0.03	0.28±0.08

2.4. Discussion

2.4.1. Fertilizer input quality rather than quantity is a prerequisite for POM accumulation

Despite different OM input quantities, all systems showed moderate increases in the fPOM (>20 μm) fraction between 1982 and 2017 (NOFERT: +0.17 mg g^{-1} ; CONMIN: +0.14 mg g^{-1} ; CONFYM: +0.16 mg g^{-1} and BIODYN: +0.16 mg g^{-1}) (**Figure 2.3a**). Significant differences for fPOM-C were only found between NOFERT and BIODYN in 1982, 1989 and 2003. This implies that the higher OM inputs from organic manures had no beneficial effect on the accumulation of fPOM, compared to CONMIN. Qualitatively, BIODYN compost was relatively enriched with more recalcitrant OM due to the higher losses of labile C compounds (Fließbach and Mäder, 2000). NMR data confirmed the higher maturity of composted manure, as fPOM A/O-A ratios in soil were highest in BIODYN (0.28), indicating a higher degree of decomposition (Baldock et al., 1997) compared to the other systems (0.23) in 2017 (**Figure S2.1 & Table 2.3**). Nevertheless, these qualitative differences did not affect the fPOM accumulation in the DOK trial. We assume that the additional input of organic fertilizers enhanced microbial activity and soil aggregation, ensuring rapid incorporation of highly labile fPOM into aggregates. Consequently, a decisive factor for the amount of fPOM at the time of soil sampling is the elapsed time since the last fertilizer application, which was at least several months in the DOK trial. As soil aggregation and thus the conversion from fPOM to oPOM can take place within a month (Bucka et al., 2019), most of the POM is expected to be mineralized or occluded within aggregates at the time of sampling, and the measured fPOM represents only the biomass input from the crop.

In contrast to the fPOM, different OM input quantities (**Table S2.2**) were manifested in the recovered oPOM-C contents. We can clearly separate systems with and without organic fertilization, as oPOM-C contents in BIODYN and CONYM were on average 46% higher than in CONMIN and NOFERT (**Figure 2.3b & Table S2.3**). OM inputs are incorporated as labile SOM fractions (Li et al., 2020; Yang et al., 2012; Zhang et al., 2021). These particles are proven to be hotspots of microbial activity (Francioli et al., 2016; Lazcano et al., 2012; Witzgall et al., 2021; Yan et al., 2007). Consequently, aggregate formation is enhanced (Cotrufo et al., 2013) e.g. through the production of extracellular polymeric substances during microbial decomposition (Costa et al., 2018), enhancing oPOM accumulation in BIODYN and CONFYM. If we compare systems without organic fertilization, we can attribute the higher oPOM-C contents in CONMIN compared to NOFERT to the mineral fertilization with the beginning of CRP 2, leading to higher biomass production and increased OM inputs from litter and crop residues. This input explains the 24% higher oPOM-C contents in CONMIN compared to NOFERT. Overall, higher A/O-A ratios of oPOM (0.31 ± 0.03) compared to fPOM (0.27 ± 0.05) (**Table 2.3**) confirm its higher degree of

decomposition (Baldock et al., 1997).

Interestingly, the 20% higher OM inputs via stacked manure in CONFYM compared to BIODYN (**Table 2.1**) were not reflected in higher oPOM-C contents. On average, oPOM was even 45% higher in BIODYN, with significant differences from 1996 onwards (**Figure 2.3b**). We assume that composted manure, also introduced considerable amounts of composting-borne microbial biomass and microbial decomposition products to the soil. Evidence can be drawn from Mäder et al. (2002) and Hartmann et al. (2015), who reported the highest microbial diversity in BIODYN plots, and Oehl et al. (2004), who found significantly higher arbuscular mycorrhizal fungi species diversity in the organic compared to the conventional farming systems of the DOK trial. In addition, Fließbach et al. (2007) reported a 25% higher microbial biomass in BIODYN compared to CONFYM plots.

Besides qualitative differences in organic manure inputs, two additional factors can contribute to the differences in oPOM-C contents between CONFYM and BIODYN: 1.) the use of pesticides in CONFYM can constrain microbial decomposition; and 2.) the additional application of mineral fertilizers in CONFYM (**Table S2.2**) may have induced positive priming through accelerated initial microbial respiration of labile C compounds (Kuzyakov et al., 2000; Moran et al., 2005; Zhou et al., 2021), that were relatively enriched in the stacked manure, compared to the composted manure. This probably contributed to the inhibiting conditions for aggregate formation and accumulation of oPOM-C in CONFYM, compared to BIODYN.

Contrary to their previous trends from 1982 to 2010, there was a strong increase in oPOM-C contents in NOFERT (62%) and CONMIN (47%), in 2017 (**Figure 2.3b**). At this time, soybean was present on the analyzed plots and green manure was incorporated into the soil in spring that year (**Table S2.1**). We assume that the implementation of soybean into the crop rotation increases N availability in the soil through biological nitrogen fixation (Stagnari et al., 2017). Therefore, crop residues can be more efficiently transformed, and in turn enhance aggregate formation (Zhou et al., 2020) and oPOM accumulation. In addition, green manure plowed in during spring before soybean cultivation represents additional OM that can be stabilized in aggregates. The trends of oPOM-C in BIODYN and CONFYM showed a highly dynamic temporal behavior with high fluctuations in each year of analysis (**Figure 2.3b**). We observed strong correlations between the extent of these fluctuations and the elapsed time between harvest and soil sampling, independent of the crop (**Figure 2.4b**). Soil sampling shortly after harvest (i.e. <14 days) led to higher oPOM-C contents, while pronounced oPOM-C losses occurred when more time elapsed between harvest and soil sampling (21 to 35 days). Harvesting interrupts biomass production (above- and belowground), abruptly reducing the supply of fresh OM to the soil. In addition, soil disturbance induces the decomposition of labile SOM fractions (Bongiorno et al., 2019). Especially the harvest of root crops affects the soil structure through mechanical stress (Panagos et al., 2019). This leads

to more atmosphere-connected soil pores (Kravchenko et al., 2015), accelerating the decomposition of previously occluded and protected SOM (Six et al., 2000). Lower OM inputs in NOFERT and CONMIN via crop residues only, led to reduced aggregate formation and thus less oPOM, and sampling timing after harvest influenced oPOM-C contents to lower degrees (**Figure 2.4a**).

To summarize, neither quantity nor quality of organic fertilizer input affected the fPOM fraction over the 36 years of observation, which rejects our hypothesized accumulation of fPOM in the systems receiving organic fertilizers. This hypothesis applies for the oPOM fraction, where, however, large annual fluctuations of oPOM-C contents in BIODYN and CONFYM clearly demonstrate its high lability, and emphasize the importance of standardized sampling dates. We assume, the quality of OM inputs rather than the quantity applied is critical here. In contrast to stacked farmyard manure (CONFYM) did composted manure (BIODYN) increase microbial activity, promote aggregate formation and oPOM accumulation. However, the potential negative impacts of mineral fertilizer and pesticide application on labile SOM fractions in CONFYM should not be neglected.

2.4.2. No additional SOC accumulation in mineral-associated fractions - regardless of fertilizer inputs

The clay-sized MAOM-C fraction (<6.3 μm) accounted for by far the largest proportion (69.4%) of the SOC across all systems, which is generally in line with observations in temperate arable soils (Christensen, 2001). NOFERT and CONMIN showed severe SOC losses of 27% and 14% respectively, while it remained stable in CONFYM (-3%) and BIODYN ($\pm 0\%$) from 1982 to 2017 (**Figure 2.5b & Table S2.3**). In CONMIN, all SOC losses from the clay-sized MAOM fraction were recorded in CRP 1, when it served as an unfertilized control system. The insufficient supply with OM inputs from crop residues during that period led to SOC losses of 15% in CONMIN. Given the high standard deviations of the individual plot replicates ($n = 4$) (**Table S2.3**), the SOC contents of the clay-sized MAOM fraction in all fertilized farming systems can be considered stable. The same holds true for the silt-sized OM fraction (63-6.3 μm), which accounted for 20.8% of total SOC averaged over all systems. Here, NOFERT showed severe SOC losses of 24%, while CONMIN, CONFYM and BIODYN remained relatively stable from 1982 to 2017 (**Figure 2.5a & Table S2.3**). Overall, the trends of all fertilized systems were uniform and SOC contents in the silt-sized OM and clay-sized MAOM fraction remained stable. Only with omission of fertilizers in NOFERT, large amounts of SOC from the mineral-associated SOC pool were lost, due to insufficient supplies with OM.

The unchanged SOC contents of the clay-sized MAOM fraction in all systems suggest that:

- 1.) the SOC storage capacity has reached saturation and/or that
- 2.) the observation period of 36 years was too short for new MAOM to form.

According to the empirical formula of Hassink (1997) and its adjustments made by Wiesmeier et al. (2015), C_{sat} of the fine fraction ($<20 \mu\text{m}$), across all analyzed DOK systems and years averaged 47.9% and 59.5%, respectively (**Figure 2.6a**). This suggests that the fine mineral fraction of the studied plots still has high C sequestration potentials (**Table S2.4**), and C sequestration deficits even increased from 1982 to 2017 in all but two BIODYN plots (**Figure 2.6b**). This contradicts assumption 1.) that clay-sized MAOM-C did not increase due to a saturation of this fraction. However, the empirical formula relies on field observations and gives only rough estimates on C saturation levels of the $<20 \mu\text{m}$ mineral fraction of DOK plots. Therefore, more detailed information on the C loading of the clay-sized MAOM fraction in the DOK trial is required, to better assess the status of C saturation. In addition, Johannes et al. (2017) observed that a decrease of SOC associated with fine mineral particles (i.e. a decrease in SOC:clay ratio), would lead to a decrease in soil structural quality, and concluded that a SOC:clay ratio of 1:10 would be a reasonable goal for soil management. As all of the studied plots had a SOC:clay ratio $<1:10$ (**Figure 2.6c & 2.6d**) which is in line with recent findings in arable soils (Prout et al., 2022), this confirms the high C sequestration potentials within the studied DOK plots. The differences in texture compared to other studies in the DOK trial are owed to sample preparation and the chosen particle size class limits (FAO) (e.g. Leifeld et al. (2009); USDA).

Confirmation for the fast incorporation of fresh OM in the MAOM fraction can be drawn from Vidal et al. (2021), who illustrated the formation of stabilized microbial-derived MAOM in micro-aggregates only 14 days after its addition to the soil. This is contradictory to assumption 2.) that OM inputs from fertilizers did not yet reach the clay-sized MAOM fraction. In addition, NMR spectra of the clay-sized MAOM-C fraction show decreasing A/O-A ratios in NOFERT from 1982 (0.65) to 2017 (0.55) (**Table 2.3**), expressing a lower degree of OM decomposition (Baldock et al., 1997). This is supported by the concomitant decrease of carboxyl C from 1982 ($13.8 \pm 0.1\%$) to 2017 ($12.6 \pm 1.1\%$), which has been observed to accumulate and stabilize in fine mineral fractions after decomposition of labile POM (Yu et al., 2015). We assume that younger (i.e. less decomposed) OM was incorporated in this fraction, accompanied by losses of older (i.e. more decomposed) OM. In BIODYN, the A/O-A ratio (0.65 to 0.62), as well as carboxyl C remained similar between 1982 ($13.1 \pm 1.2\%$) and 2017 ($13.6 \pm 0.8\%$). This means that the degree of decomposition stayed the same in BIODYN, suggesting an adequate supply of decomposed OM into the clay-sized MAOM fraction.

Root-derived C inputs represent a large share of total C inputs to arable soils and can contribute more to stable SOC fractions than aboveground crop-derived C inputs (Ghafoor et al., 2017; Kätterer et al., 2011). However, MAOM-C may be susceptible to destabilization e.g. through priming via root exudation (Jilling et al., 2021; Keiluweit et al., 2015). In the DOK trial, Hirte et al. (2018a) & Hirte et al. (2018b) showed yield-independent belowground C inputs and found similar total root biomass and

rhizodeposition between organic and conventional farming systems, under wheat, but significantly higher rhizodeposition in the organic system, under maize. This illustrates the complexity and system- and crop-dependency of root C dynamics and makes it difficult to draw accurate conclusions about the impact of belowground C inputs, especially since soil was sampled in two additional crops in this study (**Table S2.1**). In NOFERT, however, the low aboveground C inputs mean a lack of OM replenishment, which cannot compensate for potential SOC losses from the clay-sized MAOM fraction, resulting in severe losses (**Figure 2.5b**).

SOC contents of the clay-sized MAOM fraction ran on three different levels (**Figure 2.5b**). BIODYN showed the highest, CONMIN and CONFYM a medium and NOFERT the lowest level of MAOM-C contents, with significant differences recorded only between BIODYN and NOFERT from 2003 onwards (**Figure 2.5b**). We assume the different levels of SOC storage between the systems resulting from differences in clay mineralogy, which may quantitatively affect SOM stabilization. Soils of the DOK plots are dominated by 2:1 clay minerals (i.e. illite and smectite) (**Table 2.2**), that can store larger amounts of MAOM-C than 1:1 clay minerals (Barré et al., 2014; Feng et al., 2013; Six et al., 2002). The linear correlation between the proportion of illite and smectite and the amount of clay-sized MAOM-C within the studied plots emphasizes the importance of clay mineralogy for stabilization of OM inputs (**Figure 2.7**).

The fact that bulk SOC increased in BIODYN (+13.1%) and CONFYM (+4.7%) from 1982 to 2017 (**Figure 2.2**), but no additional SOC was sequestered within the clay-sized MAOM-C fraction, means that these increases were solely stored within the labile POM fractions. This result is in line with observations in fractionated topsoils from other temperate agricultural sites (Chung et al., 2008; Gulde et al., 2008) and grazed semi-arid steppe ecosystems (Steffens et al., 2011), where increased OM inputs solely led to increased SOC contents in POM fractions and macroaggregates, while fine-sized mineral fractions showed no increase. We therefore suggest that the continuous application of composted manure in BIODYN creates best conditions for enhanced microbial activity and aggregate formation and can thereby maintain SOC in the oPOM fraction at elevated levels in the long run, ensuring soil fertility. This makes oPOM a highly labile precursor for SOC storage in fine mineral fractions, dependent on OM input quality, which is in line with recent findings (Cyle et al., 2016). It also emphasizes the need for protective measures of the labile POM fractions and questions the potential of agriculturally used soils, to serve as a stable long-term C sink. Overall, our hypothesis of a steadily declining clay-sized MAOM fraction towards a new steady-state equilibrium at a lower level is only true for NOFERT, whereas the highest efficiency of C incorporation into this fraction holds true for systems receiving organic fertilizers.

2.4.3. Implications and recommendations for SOC monitoring and management

The application of organic fertilizers in the DOK trial between 1982 and 2017 resulted in a net increase of bulk SOC in BIODYN and CONFYM. However, this bulk SOC increase was exclusively measured in the labile POM fractions. Especially the highly dynamic oPOM fraction is subject to severe SOM depletion within a few days after C input halt, and sampling timing after harvest is critical for the proper measurement of the retained oPOM-C (**Figure 2.4**). Based on this observation, we recommend standardizing sampling dates to a specific narrow interval after harvest every year. This would improve the validity of C model predictions, as information on precise C observations from field trials constitute a basis for estimations on SOC dynamics, and soil management strategies are often recommended based on such models. Inconsistencies in sampling timing after harvest cause losses of information and farming system significance, regarding climate friendly soil management.

CO₂ certificates are a promotional tool in the private industry sector for the build-up of SOC stocks, setting incentives for climate mitigation (Wiesmeier et al., 2020). The increased bulk SOC concentrations in this study under organic fertilization (**Figure 2.2**) would have financially rewarded farmers in form of such certificates. However, dynamics of labile and stable SOC pools are not considered for its allocation, but only the development of bulk SOC. Based on the results of this study, a distinction between differently stable SOC pools is highly recommended, as none of the observed farming systems was sufficient to promote SOC build-up in the clay-sized MAOM-C pool. Counteracting this issue with more time-, labor- and consequently more cost-intensive laboratory analyses that account for SOM storage in differently stable SOC pools does not seem to be an adequate option.

With regards to global warming, severe SOC losses in temperate agricultural soils are projected (Wiesmeier et al., 2016), and unrealistically high amounts of additional future OM inputs and drastic management changes are needed as countermeasures (Riggers et al., 2021). POM stabilized within aggregates is the precursor for MAOM-C (Six and Paustian, 2014). Regarding the unchanged SOC contents of clay-sized MAOM fractions observed in this study (**Figure 2.5b**), we propose that the reduction of high oPOM losses (**Figure 2.3b & Figure 2.4a**) would increase the amount of OM for possible long-term storage. Therefore, the focus should be on introducing management practices, preserving this highly labile SOM pool, as a guiding paradigm for farmers to make their soils more resilient to climate change (Berthelin et al., 2022). An important lever here is to create good living conditions for soil microbes under which the transformation of the OM inputs and aggregate formation is stimulated (Witzgall et al., 2021). The application of composted manure in the BIODYN farming system was most effective in this regard. In addition, management practices that reduce aggregate turnover (e.g. reduced or no-tillage (Six and Paustian, 2014)) and enhance aggregate stability (e.g. promotion of

fungus activity (Hannula and Morriën, 2022; Six et al., 2006)) seem to be viable management options that would increase SOM persistence within agricultural soils.

2.5. Conclusions

Within this study, unfertilized and exclusively mineral fertilized farming systems showed substantial losses in bulk SOC, while the application of organic manure led to the build-up of bulk SOC, over a 36-year period. However, this build-up was solely recorded within the readily decomposable oPOM fraction and was mainly dependent on the quality of organic fertilizers (composted manure vs stacked manure). The use of composted manure without mineral fertilizer and pesticide application was most efficient. However, the oPOM fraction underlies heavy dynamics, and can be lost within a short time, consequently impeding its potential for long-term C sequestration. The fact, that no additional SOC was sequestered as MAOM from 1982 to 2017, raises concerns regarding the ability of soils to serve as a stable long-term C sink and the feasibility of climate-mitigating soil management strategies. It also emphasizes the need of continuous OM inputs to keep labile POM fractions at elevated levels, thereby maintaining soil fertility, crop performance and food security. With respect to global warming, it is likely that OM inputs would have to increase immensely to maintain current SOC stocks. In this context, it is of high importance to gain further information on the sorptive capacity and the current state of C-loading and stability of MAOM fractions, as well as turnover rates of OM inputs, which would contribute to improve SOM models. This study shows that the potential of soils to mitigate climate change has to be carefully assessed and expectations of the effect of fertilization should be low.

CHAPTER 3

Dynamic stability of mineral-associated organic matter: enhanced stability and turnover through organic fertilization in a temperate agricultural topsoil

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Abstract

Soil organic matter (SOM) plays a vital role for soil quality, sustainable food production and climate change mitigation. It is common knowledge that SOM consists of different pools with varying qualities, quantities, and turnover times. However, it is still poorly understood how mineral and organic fertilization affects the formation and stabilization of mineral-associated organic matter (MAOM) and how long it can remain there. Here, we report on the long-term effects of different farming systems on the stability and turnover of the fine silt and clay-sized MAOM fraction ($<6.3 \mu\text{m}$) of a Haplic Luvisol (0-20 cm) in the DOK long-term trial (Switzerland). We compared three farming systems with contrasting fertilization (CONMIN = pure mineral, CONFYM = mineral + organic, BIODYN = pure organic) with an unfertilized control (NOFERT) between 1982 and 2017. We performed specific surface area (SSA) measurements on fractionated MAOM samples ($<6.3 \mu\text{m}$) from 1982 and 2017, before and after removal of OM, measured the ^{14}C activity of all samples during the entire period and estimated the mean residence time (MRT) with a model taking into account 'bomb ^{14}C ' and radioactive decay. We found constant MAOM-C contents under organic fertilization. Results of SSA analysis indicate best conditions for MAOM-C stabilization under organic fertilization and different sorption mechanisms in MAOM between farming systems with and without organic fertilization. Modelled MRTs were significantly higher in NOFERT (238 ± 40 yrs) and CONMIN (195 ± 27 yrs), compared to CONFYM (138 ± 18 yrs) and BIODYN (140 ± 19 yrs), implying a high C turnover (i.e. more active MAOM) at high C contents under organic fertilization. Our findings show that MAOM is not dead OM but corroborates the concept of 'dynamic stability'. Continuous OM inputs from organic fertilizers and their rapid and constant turnover are needed to stabilize the "stable" MAOM-C fraction.

Keywords: mean residence time, specific surface area, mineral-associated organic matter, long-term trial, farming system comparison, fertilization

3.1. Introduction

Arable soils have a large potential to sequester carbon (C) as soil organic matter (SOM) (Amelung et al., 2020; Lal et al., 2018), making this process and the associated measures an attractive negative emission strategy (Paustian et al., 2019). This has prompted scientists and policy makers worldwide to promote it as a strategy for mitigating climate change (de Vries, 2018; Minasny et al., 2017).

SOM has positive effects on many physical, chemical and biological soil properties. Increasing SOM contents in arable soils enhances water holding capacity, soil structure, nutrient cycling and microbial diversity (Lal, 2020; Rabot et al., 2018; Weil and Magdoff, 2004), improving soil fertility and soil health (Bünemann et al., 2018), and consequently contributing to sustainable crop production and food security (Lal, 2010). By improving soil structure, SOM promotes infiltration and retention of water, thus ensuring soil functions in the face of increasing weather extremes (e.g. droughts) (Kundel et al., 2020).

Anthropogenic climate change is predicted to accelerate the already severe SOM losses (Riggers et al., 2021; Wiesmeier et al., 2016) brought on by land use change and agricultural management (Paustian et al., 2016; Sanderman et al., 2017). Accordingly, it is essential to implement agricultural practices that increase the transfer of atmospheric C to the soil and prevent its rapid release, i.e. promote long-term C storage in the soil as SOM. The application of organic fertilizers is known to enhance SOM contents compared to mineral fertilization (Gattinger et al., 2012; Krause et al., 2022). While fertilizer type (i.e. mineral vs. organic) and qualitative differences between organic fertilizers have shown to be decisive for the accumulation of labile OM (Mayer et al., 2022a), their effects on the stable OM fractions remain poorly understood. Therefore, estimating the duration of C storage and understanding the underlying soil processes under contrasting fertilization, especially over long-term periods, is of great interest for the design of the respective measures.

The persistence of SOM, i.e. SOM longevity as a result of the interactions with its chemical, physical and biological environment (Schmidt et al., 2011), can be expressed as mean residence time (MRT). The estimation of MRT is often based on isotopic approaches. Among these, radiocarbon analysis is a unique technique that enables the determination of C dynamics in soils on decadal to millennial timescales (Paul et al., 1997; Trumbore, 2009; Wang and Hsieh, 2002). In mineral soils, MRT of SOM largely depends on organo-mineral interactions, which are driven by specific stabilization mechanisms. Sorption of SOM onto surfaces of fine-sized mineral particles following microbial transformation is considered a dominant mechanism responsible for the formation of a stable mineral-associated OM (MAOM) fraction (Cotrufo et al., 2013; Newcomb et al., 2017; Schmidt et al., 2011). Over time, the gradual formation of organo-mineral complexes and microaggregates (Totsche et al., 2018) spatially separates SOM from microbes and enzymes. This limits its further decay through reduced accessibility and oxygen supply, ultimately

increasing the MRT to time-scales of centuries to millennia (Kleber et al., 2015; Kögel-Knabner et al., 2008b; Six et al., 2002; von Lützow et al., 2006).

Reactive surfaces of fine mineral particles stabilize the majority of organic C in many mineral soils (Kramer and Chadwick, 2018), but the size of these surfaces varies for different phyllosilicates (Kleber et al., 2021). Therefore, soil mineralogy has a major influence on the SOM stabilization potential (Barré et al., 2014; Feng et al., 2013). However, the dynamic nature and reversibility of this binding mechanism has been described (Kleber et al., 2021; Kuzyakov et al., 2000; Steffens et al., 2009), defying the long-held belief that adsorption to fine mineral surfaces would put a stop to the cycling of affected SOM. In addition, studies dealing with OM storage in differently stable SOM fractions even indicate that this stable MAOM is not increased but only kept stable under specific agricultural practices (Chung et al., 2008; Gulde et al., 2008; Steffens et al., 2011). An improved knowledge of the involved mechanisms will thus allow to better evaluate farming systems in terms of their effectiveness for the long-term storage of atmospheric CO₂ as SOM, thereby maintaining soil quality and contributing to climate mitigation via climate-smart agricultural practices (Paustian et al., 2016).

The objective of this study was to assess the long-term effect of different farming systems on the stability of fine silt and clay-sized MAOM (<6.3 µm; 0-20 cm depth), in the DOK long-term experiment (Therwil, CH) (Mäder et al., 2002). Our study focused on four farming systems: an organic system using only organic manure (BIODYN), two conventional systems, one using only mineral fertilizer (CONMIN) and the other combining the use of mineral fertilizer and farmyard manure (CONFYM), and an unfertilized control (NOFERT). Recent results on the long-term development of bulk SOC (<2 mm) show an increase in BIODYN, no change in CONFYM and decreases in CONMIN and NOFERT (Krause et al., 2022). However, no quantitative changes of MAOM were measured over a 36-year period, regardless of fertilizer quality within the farming systems (Mayer et al., 2022a).

We hypothesize, that (i) long-term organic fertilizer application (CONFYM and BIODYN) initiates higher stability of MAOM through enhanced microbial activity and diversity, and as a result (ii) this would translate to longer MRTs than in farming systems with pure mineral (CONMIN) or without any fertilizer application (NOFERT). To test this hypothesis, we measured changes in SSA via N₂ adsorption and took advantage of ¹⁴C radiocarbon analyses to elucidate the turnover dynamics within MAOM by means of MRT estimation.

3.2. Materials and Methods

3.2.1. Experimental setup and sample selection

The DOK farming system comparison trial is located in Therwil (canton of Basel Landschaft, Switzerland, 47°30' N, 7°32' E) and was initiated in 1978 (Mäder et al., 2002). Here, organic and conventional farming systems are compared under temperate climatic conditions (10.5°C mean annual temperature; 840 mm mean annual precipitation; (Krause et al., 2020)). The soil is a Haplic Luvisol (WRB, 2015), developed on deposits of alluvial loess, with 3% sand, 76% silt and 21% clay (Mayer et al., 2022a).

The experiment has a split-plot design, each farming system is replicated in four columns, and subject to the same seven-year crop rotation (crop rotation period = CRP) with two years of grass-clover ley (see **Table S2.1**), temporally shifted in three subplots. All farming systems have the same type of tillage (moldboard plowing, 0-20 cm), but receive different types of plant protection (see **Table 2.1**). We focused on four farming systems with different fertilizer types and quantities within the six completed CRP (CRP 1 = 1978-1984, CRP 2 = 1985-1991, CRP 3 = 1992-1998, CRP 4 = 1999-2005, CRP 5 = 2006-2012 and CRP 6 = 2013-2019). NOFERT is the unfertilized control. CONMIN is conventionally managed, and receives mineral fertilizer only (unfertilized in CRP 1). CONFYM is an integrated conventional system, with combined mineral and organic fertilizer application. BIODYN is an organic, biodynamically managed farming system that receives only organic fertilizer.

In CONFYM (stacked farmyard manure and slurry) and BIODYN (composted manure and slurry), the addition of organic fertilizer is equivalent to the manure and slurry produced by 1.4 livestock units ha⁻¹ yr⁻¹. Farming system-specific preparation of raw manures (CONFYM = manure stacking, BIODYN = aerobic composting) led to quantitative and qualitative differences at the time of its application. In addition, slurry is added to meet the nutrient requirements of the respective crop (mainly N). In CONMIN and CONFYM, mineral fertilizers are added up to the limits of Swiss fertilization recommendations (Richner and Sinaj, 2017). Because farmyard manure N inputs are not fully accounted for as readily bioavailable, N inputs are higher in CONFYM than in CONMIN (see **Table S2.2**). After harvest, straw biomass was removed from the plots. Over the observational period from 1982 to 2017, annual OM inputs via manure and slurry to the analyzed plots in subplot B (**Figure S3.1**) averaged 2508 (CONFYM) and 2000 kg dry matter ha⁻¹ yr⁻¹ (BIODYN). Organic and conventional farming systems of the DOK trial have yield-independent belowground C inputs, as well as similar total root biomass and rhizodeposition for the crops present on the analyzed plots in this study (Hirte et al., 2018a; Hirte et al., 2018b). After harvest, straw biomass was removed from the plots.

We used air-dried (40°C) and sieved (<2 mm) bulk soil samples from the DOK soil sample archive at Agroscope Reckenholz. These were taken from 16 plots (subplot B, **Figure S3.1**) in the same year within each completed CRP (1982, 1989, 1996, 2003, 2010 and 2017) (see **Table S2.1**) after harvest with a soil corer (0-20 cm depth). This totaled 96 soil samples (four farming systems x four replicates x six CRPs).

3.2.2. Clay content and clay mineralogy

Texture of bulk soil samples (<2 mm) was measured with the PARIO Plus Soil Particle Analyzer (METER Group, Germany/USA). Prior to measurement, OM was removed from 25-30 g of soil via oxidation (12 h) with hydrogen peroxide (H₂O₂, 30%). Subsequently, H₂O₂ was removed from the sample by rinsing with deionized water, centrifuging and decanting until an electrical conductivity of <400 µS m⁻¹. Sodium hexametaphosphate (Na₆O₁₈P₆) was used for sample dispersion.

Mineralogy of the clay fraction (<2 µm) was determined using powder X-ray diffraction (P-XRD, Cubix³, Malvern Panalytical, Almelo, Netherlands). Prior to analysis, samples were treated with hydrochloric acid (HCl) to remove OM. P-XRD was performed on random powder samples and on oriented samples after saturation with Ca²⁺ and ethylene glycol (room temperature) and K⁺ (room temperature and stepwise heated to 550 °C).

3.2.3. Physical fractionation

We followed a modified density and particle size fractionation scheme of Kölbl and Kögel-Knabner (2004) and Steffens et al. (2009) to separate POM and MAOM fractions from bulk soils. A detailed description of the fractionation procedure can be found in Mayer et al. (2022a). Briefly, POM fractions (>20 µm), i.e. free particulate OM (fPOM) and occluded particulate OM (oPOM), were separated via density fractionation in a Na-polytungstate solution ($\rho = 1.8 \text{ g cm}^{-3}$) before and after aggregate disruption through ultrasonication (200 J ml⁻¹), from 30 g of air-dried bulk soil (<2 mm). The remaining mineral fraction was rinsed salt-free and separated by wet sieving and sedimentation in Atterberg cylinders to yield the fine silt and clay-sized MAOM fraction (<6.3 µm) (Mueller et al., 2014).

All separated SOM fractions were air-dried at 60°C, ground and analyzed in duplicate for total C concentrations via dry combustion on a Vario EL cube elemental analyzer (Elementar Analysensysteme, Hanau, Germany). As bulk samples were free of carbonates, the total C concentration equals the organic C concentration.

3.2.4. Specific surface area analysis

We measured the specific surface area (SSA) of the MAOM fraction from 1982 and 2017 by multiple-point BET (Brunauer et al., 1938) adsorption of N₂ at 77 K, using the BELSORP®-miniX surface area and pore size distribution analyzer (Microtrac MRB, USA/Japan/Germany), each before (SSA_{untreated}) and after removal of OM (SSA_{NaOCl}). Prior to measurement, samples were outgassed for 6-12 h under vacuum at 75°C. After SSA_{untreated} measurement, OM was removed from the same samples following a modified method of Kaiser et al. (2002) and Zimmermann et al. (2007). Briefly, 0.7-1 g of sample was oxidized during 18 h at room temperature (25°C) with 6% sodium hypochlorite (NaOCl). We adjusted the solution to pH 8 with concentrated hydrochloric acid (HCl), at a soil-to-solution ratio of 1:50 (wt/wt). The samples were then centrifuged at 2000 g for 30 min and rinsed with deionized water until <50 µS cm⁻¹. OM oxidation and rinsing was repeated three times. Afterwards the SSA was determined again for the treated samples (SSA_{NaOCl}).

3.2.5. Radiocarbon analysis

The ¹⁴C activity of OC in the separated MAOM fraction (<6.3 µm) of all plots and sampled years (n = 16 x 6 = 96) was measured with accelerator mass spectrometry (AMS) at the Laboratory for the Analysis of Radiocarbon with AMS (LARA) at the University of Bern (Szidat et al., 2014). Without any further chemical treatment, roughly 30 mg of ground and homogenized sample material (≅ 1 mg C) was combusted in an elemental analyzer (Vario Micro Cube, Elementar Analysensysteme, Hanau, Germany), transformed into solid targets using an automated graphitization equipment (AGE), and measured with the MIni Carbon DAting System MICADAS (Synal et al., 2007). Each AMS measurement included multiple OxII radiocarbon standards (NIST, SRM 4990 C) and fossil sodium acetate samples for normalization and correction of blanks as well as isotopic fractionations.

3.2.5.1. Mean residence time (MRT) of MAOM

The mean residence time (MRT) of MAOM was calculated using a ¹⁴C model that takes into account 'bomb ¹⁴C' and radioactive decay (Conen et al., 2008; Mueller et al., 2014). First, we determined the ¹⁴C activity (Fraction Modern; F¹⁴C) of OC, following the approach of Harkness et al. (1986):

$$A_t = A_{(t-1)} * e^{-k} + (1 - e^{-k}) * A_i - A_{(t-1)} * \lambda \quad (1)$$

where A_t is the measured ¹⁴C activity in MAOM at time t , i.e. the respective year of soil sampling, corrected for radioactive decay until the year of ¹⁴C measurement (2021). $A_{(t-1)}$ is the ¹⁴C activity of SOM in the year preceding sampling, k the exchange rate of OC in MAOM (i.e. 1/MRT), and λ the ¹⁴C decay constant (1/8268 yr⁻¹). A_i is the ¹⁴C activity within the atmosphere and is composed of data from Reimer

et al. (2020) (1511-1950) and Hua et al. (2022) (1950-2017).

A fundamental requirement of the model is the steady-state condition of the investigated fraction, i.e. balanced C inputs and outputs. In BIODYN and CONFYM, the MAOM-C content was in steady-state from 1982 to 2017, and in CONMIN and NOFERT from 1989 to 2017 and from 2003 to 2017, respectively (**Table S3.1**). This meant that MRTs had to be estimated based on ^{14}C activities of different periods within the farming systems. Therefore, we additionally used the period from 2003 to 2017, during which MAOM-C contents of all farming systems were in steady-state.

We calculated the MRT of OM in MAOM according to equation (1) by repeatedly adjusting the MRT until the root-mean-square error (RMSE) between the calculated A_i at the chosen MRT and the measured ^{14}C activity at the corresponding sampled years reached the minimum. However, there is an unknown time difference between C assimilation by the crop and OM incorporation into MAOM (i.e. time lag). Therefore, we tested different time lags (0, 5 and 10 years), to account for the change in ^{14}C signal of the incoming OM caused by radioactive decay during this period, which affects the estimation of the MRT.

3.2.5.2. Carbon turnover rates within MAOM

We calculated the annual C turnover rate in MAOM ($\text{mg g}^{-1} \text{yr}^{-1}$) for each plot by dividing the mean MAOM-C content (mg g^{-1}) during steady-state periods (NOFERT: 2003-2017, CONMIN: 1989-2017, CONFYM and BIODYN: 1982-2017) by the estimated MRT. In addition, we multiplied the annual MAOM-C turnover rate of each plot with its soil volume per hectare (0-20 cm depth) (using bulk densities of CRP 1, assuming its consistency over time (Leifeld et al., 2009)) to obtain values in a physical unit relevant to practice ($\text{kg C ha}^{-1} \text{yr}^{-1}$).

3.2.6. Statistical analyses

We used a one-way ANOVA in RStudio (R version 4.1.2.; RStudio Team (2021)) to identify statistically significant differences between farming systems for SSA, estimated MRTs and turnover rates. Prior to the ANOVA, residuals were tested for normal distribution using the Shapiro-Wilk test and visual inspection of QQ-plots, and homogeneity of variances was tested using Levene's test. Subsequently, a post-hoc Tukey HSD test was performed using a significance level of $\alpha = 0.05$, for all tests.

We applied a linear mixed effects model with repeated measurements to determine the impact of farming systems on ^{14}C activities and OC removal (i.e. oxidation-resistant and removable OC) as a function of sampling year. In short, the lme function of the nlme package was used (Pinheiro et al., 2020) with farming system nested in subplot and column as repeated random factors to account for spatial heterogeneity within the experimental design of the DOK trial. A two-way ANOVA was then employed

to determine the impact of farming system, sampling year and their interaction on ^{14}C activities. Residuals were tested for normal distribution using the Shapiro-Wilk test and visual inspection of QQ-plots, and homogeneity of variances was tested using Levene's test. Subsequently, a post-hoc Tukey HSD test was performed using a significance level of $\alpha = 0.05$, to test for differences between the farming systems.

3.3. Results

3.3.1. Clay content, mineralogy and development of MAOM-C contents

Clay content (<2 μm) was similar between all farming systems and averaged $21.5 \pm 3.2\%$. Clay mineralogy was dominated by 2:1 phyllosilicates, i.e. Illite ($12.6 \pm 3.1\%$) and Smectite ($3.7 \pm 1.7\%$) (**Table 3.1**). Within NOFERT, CONMIN and BIODYN there was one plot each (plot 93, 94 and 88) that had higher clay contents and Illite and/or Smectite contents compared to the other three plot replicates within the farming system.

Table 3.1: Overview of clay characteristics of all 16 observed plots, measured on bulk soil samples from 2019. Values in bold indicate mean values and standard deviations of the 4 plots per farming system. A one-way ANOVA revealed no significant differences between any of the farming systems for any parameter.

farming system	plot	clay (<2 μm) [%]	phyllosilicates [%]	2:1		1:1	
				Illite [%]	Smectite [%]	Chlorite [%]	Kaolinite [%]
NOFERT	3	19.5	21.6	11.7	4.6	4.3	1.0
	37	15.5	18.0	10.9	2.7	3.5	0.9
	59	21.1	18.6	11.3	2.7	4.5	0.1
	93	24.8	21.7	8.6	7.3	2.7	3.0
			20.2\pm3.4	20.0\pm2.0	10.6\pm1.4	4.3\pm2.2	3.8\pm0.8
CONMIN	4	21.9	20.8	12.9	3.1	2.9	1.9
	38	20.7	19.4	10.9	4.2	2.0	2.3
	60	19.9	15.7	8.0	4.1	1.8	1.9
	94	24.3	26.3	16.9	3.9	4.3	1.3
			21.7\pm1.9	20.6\pm4.4	12.2\pm3.7	3.8\pm0.5	2.8\pm1.1
CONFYM	22	21.4	17.5	11.4	2.5	3.2	0.4
	32	16.5	21.0	14.7	2.6	3.1	0.6
	66	22.4	20.4	14.1	2.4	3.7	0.3
	76	21.2	21.5	14.4	2.6	3.4	1.1
			20.4\pm2.6	20.1\pm1.8	13.7\pm1.5	2.5\pm0.1	3.4\pm0.3
BIODYN	10	21.7	24.7	12.1	7.6	2.4	2.6
	44	21.7	17.5	11.5	2.1	2.0	1.9
	54	21.3	16.9	11.5	1.8	2.2	1.4
	88	29.3	31.5	21.0	4.2	2.6	3.7
			23.5\pm3.9	22.7\pm6.9	14.0\pm4.7	3.9\pm2.7	2.3\pm0.3

Detailed results on the distribution of C between the separated fractions and their temporal development can be found in Mayer et al. (2022a). In BIODYN and CONFYM, MAOM-C contents remained stable over the whole observation period (**Table S3.1**). In CONMIN, MAOM-C contents decreased by 14% from 1982 to 1989, but remained stable thereafter. In NOFERT, MAOM-C contents decreased by 27% from 1982 to 2003, but remained stable thereafter. Throughout the whole observation period, CONFYM and CONMIN had similar MAOM-C levels. The only significant differences in MAOM-C contents were measured between BIODYN and NOFERT from 2003 onwards.

3.3.2. Specific surface area analysis

In 1982, $SSA_{\text{untreated}}$ of MAOM was similar in all farming systems, averaging $17.1 \pm 1.8 \text{ m}^2 \text{ g}^{-1}$ (**Figure 3.1** and **Table 3.2**). $SSA_{\text{untreated}}$ remained constant in 2017 in all farming systems except NOFERT, where it increased significantly. This increase occurred only when excluding an extreme outlier (plot 93, marked with asterisk in **Figure 3.1**), which showed a strong decrease of $-6.2 \text{ m}^2 \text{ g}^{-1}$ from 1982 to 2017 and had by far the highest clay content (24.8%) compared to the other NOFERT plots (**Table 3.1**).

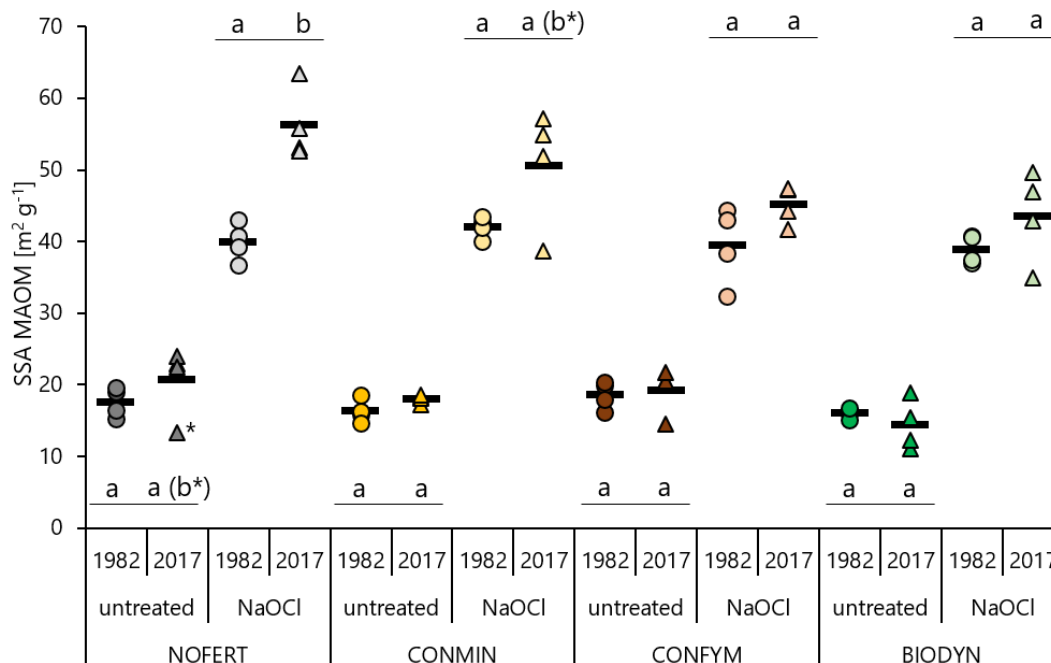


Figure 3.1: Specific surface area (SSA) of MAOM determined by multiple-point BET adsorption of N_2 . Symbols show single plot replicates ($n = 4$) for each farming system from the first year (1982, circles) and last year of sampling (2017, triangles). Dark and light shades show untreated samples and samples after OC removal with NaOCl, respectively, color-coded according to each farming system. Black bars represent the mean of 4 plot replicates and post-hoc Tukey letters give significant differences at $p < 0.05$. Single plot replicates with asterisks are outliers within the farming systems. Post-hoc Tukey letters in brackets give the significant differences when excluding outliers.

Across all plots and years, the efficiency of OC removal as the relative proportion of initial OC in MAOM ranged from 62 to 82% which is consistent with results of other studies that also used NaOCl (Helfrich et al., 2007; Mikutta and Kaiser, 2011; Mikutta et al., 2005). In 1982, the average OC removal via NaOCl was $5.4 \pm 0.8 \text{ mg g}^{-1}$ ($= 69.5 \pm 2.8\%$ of total MAOM-C) with no significant differences between the farming systems (**Figure 3.2** and **Table 3.2**). The amount of oxidation-resistant OC was also similar across farming systems. The removal of OC significantly increased the measured SSA (SSA_{NaOCl}) by $22.99 \text{ m}^2 \text{ g}^{-1}$ on average to a mean of $40.1 \pm 3.2 \text{ m}^2 \text{ g}^{-1}$, with no significant differences among farming systems.

In 2017, oxidation-resistant OC significantly decreased in NOFERT and slightly decreased in CONMIN, compared to 1982. In CONFYM and BIODYN, the amount of oxidation-resistant OC remained unchanged from 1982 to 2017 (**Figure 3.2** and **Table 3.2**). SSA_{NaOCl} increased significantly more than after NaOCl

treatment in 1982 ($+30.8 \text{ m}^2 \text{ g}^{-1}$) to an average of $48.9 \pm 7.4 \text{ m}^2 \text{ g}^{-1}$ across all systems (**Figure 3.1** and **Table 3.2**).

Per milligram OC removed by NaOCl, an average of $4.4 \pm 0.9 \text{ m}^2$ of SSA was exposed in 1982, with no significant differences between farming systems (**Table 3.2**). In 2017, the SSA exposed per milligram of removed OC increased to a mean of $6.5 \pm 2.0 \text{ m}^2$ (NOFERT: $+3.9$, CONMIN: $+2.0$, CONFYM: $+1.2$ and BIODYN: $+1.1 \text{ m}^2 \text{ mg}^{-1}$) with significant increases in NOFERT.

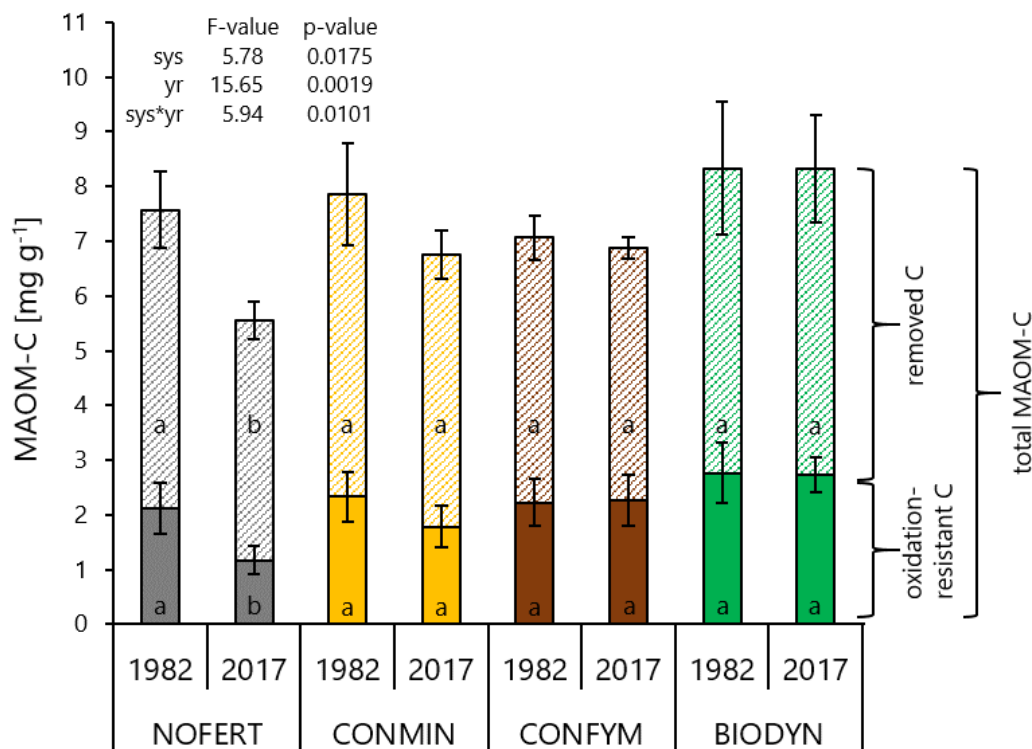


Figure 3.2: Efficiency of C removal in MAOM in all farming systems via treatment with NaOCl for the first (1982) and last year (2017) of observation. Filled columns show the C proportion that was not removed by NaOCl, i.e. resistant to oxidation, and shaded columns show the C proportion that was removed by NaOCl. Error bars show the standard deviation of the individual plots ($n = 4$) per farming system. Results of a repeated two-way ANOVA (sys = farming system, yr = year) are depicted, using a linear mixed effect model that accounts for the spatial arrangement of plots within the experimental design. Post-hoc Tukey letters give significant differences between 1982 and 2017 at $p < 0.05$.

Table 3.2: Overview of OC removal efficiency and SSA analyses of each farming system for the first year (1982) and last year of observation (2017), before ($SSA_{untreated}$) and after (SSA_{NaOCl}) treatment with NaOCl. $SSA_{NaOCl} - SSA_{untreated}$ corresponds to the mineral surface area exposed after OC removal and $\Delta SSA / OC$ removed corresponds to the mineral surface area exposed per mg of OC removed. The values correspond to the mean of $n = 4$ plots per farming system and their standard deviation. Significant differences between systems at $p < 0.05$ are indicated by post-hoc Tukey letters. Post-hoc Tukey letters in brackets give the significant differences excluding outliers.

year	farming system	OC removal		oxidation-resistant OC	$SSA_{untreated}$	SSA_{NaOCl}	$SSA_{NaOCl} - SSA_{untreated}$	$\Delta SSA / OC$ removed
		$[mg\ g^{-1}]$	[%]					
1982	NOFERT	5.45 ± 0.70 a	72.1 ± 2.2	2.13 ± 0.47 a	17.47 ± 2.06 a	39.89 ± 2.67 a	22.42 ± 2.93 a	4.19 ± 0.93 a
	CONMIN	5.52 ± 0.94 a	70.3 ± 2.1	2.34 ± 0.45 a	16.28 ± 1.64 a	42.01 ± 1.52 a	25.73 ± 2.47 a	4.73 ± 0.75 a
	CONFYM	4.84 ± 0.41 a	68.7 ± 2.2	2.23 ± 0.43 a	18.56 ± 1.90 a	39.48 ± 5.54 a	20.92 ± 3.60 a	4.39 ± 1.10 a
	BIODYN	5.57 ± 1.21 a	66.8 ± 2.3	2.76 ± 0.55 a	16.00 ± 0.71 a	38.90 ± 2.02 a	22.90 ± 1.55 a	4.28 ± 1.11 a
2017	NOFERT	4.37 ± 0.34 a	79.0 ± 2.4	1.18 ± 0.25 a	20.62 ± 4.95 a (a*)	56.19 ± 5.02 a (a*)	35.56 ± 9.77 a	8.11 ± 1.93 a
	CONMIN	4.97 ± 0.46 ab	73.8 ± 2.7	1.78 ± 0.38 ab	17.97 ± 0.58 a (ab*)	50.62 ± 8.28 a (a*)	32.65 ± 8.60 a	6.71 ± 2.20 a
	CONFYM	4.61 ± 0.19 ab	67.3 ± 4.9	2.26 ± 0.47 bc	19.18 ± 3.21 a (ab*)	45.11 ± 2.70 a (b*)	25.93 ± 4.87 a	5.61 ± 1.00 a
	BIODYN	5.60 ± 0.99 b	67.1 ± 2.6	2.73 ± 0.32 c	14.34 ± 3.51 a (b*)	43.51 ± 6.40 a (b*)	29.17 ± 9.89 a	5.42 ± 2.18 a

3.3.3. Carbon mean residence times

In all farming systems, the average ^{14}C activity of MAOM (Fraction Modern, $F^{14}\text{C}$) significantly decreased from 1.0589 in 1982 to 1.0205 in 2017, and was significantly affected by sampling year and farming system (**Figure 3.3**). It is noticeable that systems without organic fertilizer (NOFERT and CONMIN) and systems with organic fertilizer application (CONFYM and BIODYN) show significantly different ^{14}C activities from 1996 onwards. On average, ^{14}C activity was 0.0214 $F^{14}\text{C}$ higher in CONFYM and BIODYN compared to CONMIN and NOFERT.

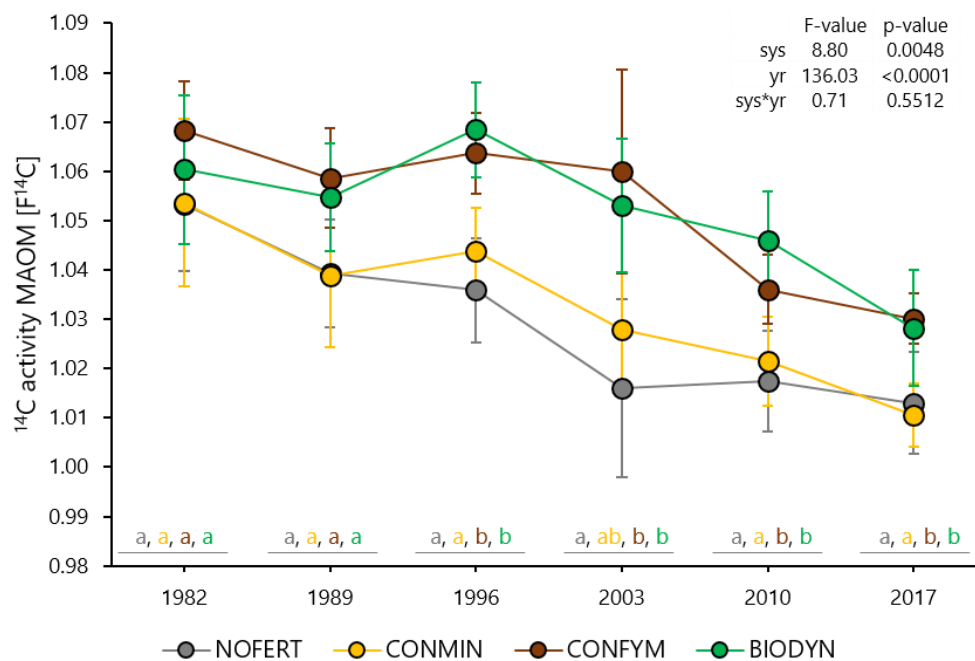


Figure 3.3: ^{14}C activity, given in Fraction Modern ($F^{14}\text{C}$) measured within MAOM for all farming systems and sampled years. Circles show farming system means and the error bars show the standard deviation of single plot replicates ($n = 4$) per farming system. Results of a repeated two-way ANOVA (sys = farming system, yr = year) are depicted, using a linear mixed effect model that accounts for the spatial arrangement of plots within the experimental design. Post-hoc Tukey letters give significant differences at $p < 0.05$.

The basic model requirement for the MRT estimation was the steady-state condition of MAOM. We had to choose a time lag (between C assimilation by the crop until incorporation in MAOM) and a period for the estimation of MRT (steady-state period for each individual farming system, or due to better comparability, the steady-state period of NOFERT (2003-2017) for all farming systems). Estimated MRT were found to be robust in a sensitivity analysis, regarding the order of farming systems for all tested time lags and periods (**Figure S3.2** and **Table S3.2**). The 10-yr time lag was excluded due to high RMSE (steady-state: 0.0194, 2003-2017: 0.0242). The 0-yr time lag had relatively low RMSE (steady-state: 0.0133, 2003-2017: 0.0098), but would imply that there was no temporal offset between C assimilation by the crop and incorporation of OM into MAOM, which is unlikely and would affect the MRT estimation. Finally, we chose a 5-yr time lag and the individual steady-state periods of the farming systems (**Table**

S3.2) to account for higher amounts of observations (steady-state: $n = 80$, 2003-2017: $n = 48$) instead of minimal improvements in model accuracy (RMSE; steady-state: 0.0107, 2003-2017: 0.0102). The estimated MRTs of MAOM averaged 178 ± 49 yrs across all farming systems and were significantly higher in NOFERT (238 ± 40 yrs) and CONMIN (195 ± 27 yrs), compared to CONFYM (138 ± 18 yrs) and BIODYN (140 ± 19 yrs) (**Figure 3.4a**).

We identified one outlier plot in both, NOFERT and CONMIN (marked with an asterisk in **Figure 4a**). The NOFERT outlier (plot 37) had a significantly lower clay content (15.5%), as well as the lowest calculated MRT compared to the other NOFERT plots. In contrast, the CONMIN outlier (plot 94) had the highest clay content (24.3%), as well as the highest calculated MRT, compared to the other CONMIN plots. In addition, we observed a positive correlation between the calculated MRT and clay content, especially for farming systems not receiving organic fertilizers (R^2 : NOFERT = 0.85, CONMIN = 0.83) (**Figure 5a**). We also found a strong positive correlation between the estimated MRT and smectite contents (**Figure 5b**).

3.3.4. Carbon turnover rates within MAOM

The amount of MAOM-C that passes annually through this fraction during steady-state periods averaged $0.043 \text{ mg C g}^{-1} \text{ yr}^{-1}$. It was lowest in NOFERT ($0.024 \pm 0.003 \text{ mg C g}^{-1} \text{ yr}^{-1}$), followed by CONMIN ($0.034 \pm 0.003 \text{ mg C g}^{-1} \text{ yr}^{-1}$), CONFYM ($0.051 \pm 0.009 \text{ mg C g}^{-1} \text{ yr}^{-1}$) and highest in BIODYN ($0.059 \pm 0.004 \text{ mg C g}^{-1} \text{ yr}^{-1}$) (**Figure 3.4b, bottom right**). We found no significant differences between CONFYM and BIODYN, but their C turnover was significantly higher than in CONMIN and NOFERT, and significantly higher in CONMIN than in NOFERT. This corresponded to an average annual C mass flow rate in MAOM of $111 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (0-20 cm) across farming systems (NOFERT: $62 \pm 8 < \text{CONMIN: } 91 \pm 6 < \text{CONFYM: } 137 \pm 22 < \text{BIODYN: } 155 \pm 11 \text{ kg C ha}^{-1} \text{ yr}^{-1}$) (**Figure 3.4b**).

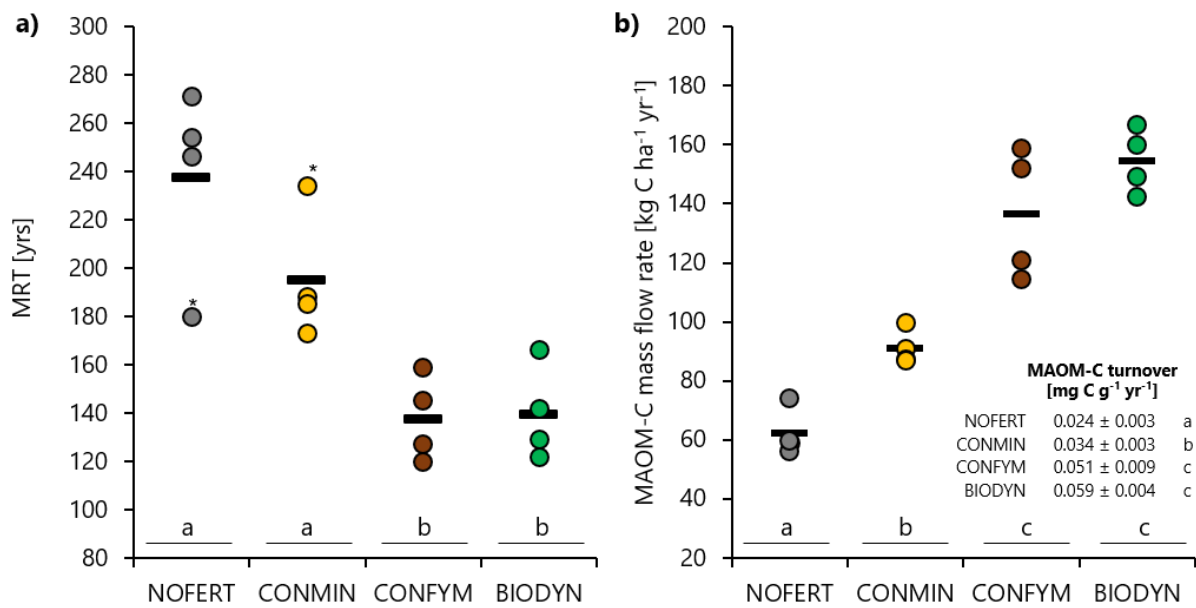


Figure 3.4: **a)** Estimated mean residence times (MRT, yrs) of MAOM for each farming system (5-yr time lag) and **b)** annual C mass flow rate ($\text{kg C ha}^{-1} \text{yr}^{-1}$) during steady-state periods within each farming system (NOFERT: 2003-2017, CONMIN: 1989-2017, CONFYM and BIODYN: 1982-2017). The black bars represent the mean values per farming system of $n = 4$ individual plot replicates, depicted as colored circles. Post-hoc Tukey letters give significant differences at $p < 0.05$ between farming systems after one-way ANOVA. Single plot replicates marked with an asterisk show outliers.

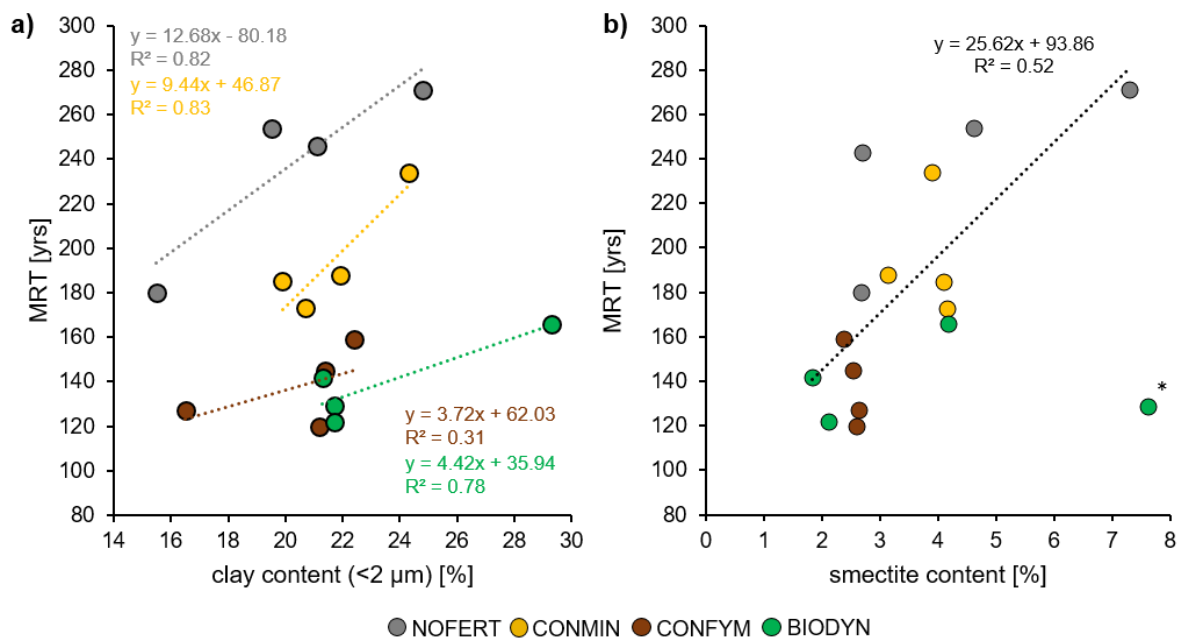


Figure 3.5: Correlation of estimated MRT (yrs) of MAOM with **a)** clay content ($< 2 \mu\text{m}$) and **b)** smectite content. Circles show the single plot replicates and dotted lines show the linear trends of the circles colored according to the respective farming system. In **b)**, the linear trend over all plots is shown, excluding the outlier marked with an asterisk.

3.4. Discussion

3.4.1. Best preconditions for MAOM-C stabilization under pure organic fertilization

In 1982, oxidation of OM with NaOCl resulted in an equal increase of SSA_{NaOCl} (**Figure 3.1**) and similar amounts of oxidation-resistant C (**Figure 3.2**) in all farming systems. In 2017, SSA_{NaOCl} significantly increased in NOFERT and CONMIN (**Figure 3.1**), and oxidation-resistant C significantly decreased in NOFERT, compared to treated samples from 1982 (**Table 3.2** and **Figure 3.2**). This suggests that 36 years of arable farming negatively affected the stability of OM in MAOM in these systems.

Oxidation-resistant C is typically found in organo-mineral associations (Eusterhues et al., 2003; Mikutta et al., 2006), i.e. building units of microaggregates (Totsche et al., 2018). Microaggregates are formed within macroaggregates (Oades and Waters, 1991). Therefore, macroaggregate formation and turnover is a major determinant of MAOM stability (Six et al., 2000), but is negatively influenced by tillage and harvesting practices (Mayer et al., 2022a). Organic fertilization in BIODYN and CONFYM significantly increased the microbial activity (Krause et al., 2022), which led to increased aggregate formation, relative to NOFERT and CONMIN (Mayer et al., 2022a). In BIODYN and CONFYM, this resulted in unchanged amounts of oxidation-resistant MAOM-C at higher levels than in CONMIN and NOFERT, where oxidation resistant MAOM-C was reduced from 1982 to 2017 (**Figure 3.2**).

NaOCl treatment increased the exposure of mineral surface area per mg of destroyed OC in 2017, compared to treated samples in 1982 (**Table 3.2**). In BIODYN ($5.42 \pm 2.18 \text{ m}^2 \text{ g}^{-1}$) and CONFYM ($5.61 \pm 1.00 \text{ m}^2 \text{ g}^{-1}$), less SSA was exposed compared to CONMIN ($6.71 \pm 2.20 \text{ m}^2 \text{ g}^{-1}$) and the significant increase in NOFERT ($8.11 \pm 1.93 \text{ m}^2 \text{ g}^{-1}$) (**Table 3.2**). These results indicate a reduced aggregate stability, especially under low OM inputs (i.e. NOFERT and CONMIN), which allowed NaOCl to increasingly enter and break up previously more stable aggregates, exposing surface areas that were not accessible in 1982. In addition, this could indicate a shift of C sorption from organo-organic associations (i.e. C patches) to organo-mineral associations (i.e. directly on the mineral surface) (Kleber et al., 2015; Vogel et al., 2014) in CONMIN and NOFERT. In BIODYN and CONFYM however, new OM from fertilizers might preferentially form patchy organo-organic assemblages, where OM is already present (Possinger et al., 2020; Vogel et al., 2014). Therefore, we assume that in systems with regular OM supply via organic fertilization, its stabilization in MAOM is largely decoupled from the availability of free binding sites on fine mineral particle surfaces (Schweizer et al., 2018).

It is noteworthy, that the qualitative differences between the applied organic fertilizers (BIODYN = composted manure; CONFYM = stacked manure) did not affect OM stabilization in MAOM (**Figure 3.1**,

Figure 3.2 and **Table S3.1**). This was despite the relative enrichment of BIODYN compost with more recalcitrant plant-derived OM and microbial degradation products due to the higher losses of labile C compounds during aerobic composting (Fließbach and Mäder, 2000), compared to stacked manure in CONFYM. Previous fractionation results with the same samples showed significant differences in aggregate formation and oPOM quantity between these two farming systems as a consequence of different fertilizer qualities (Mayer et al., 2022a). So, this would have been expected to affect MAOM-forming processes via more direct contacts between organic fertilizers and mineral surfaces. However, we assume that 1.) the qualitative differences were too subtle (C/N 17 in BIODYN vs. 23 in CONFYM) (**Table S2.2**); and 2.) the differences were neutralized during the transition, i.e. continuous degradation from the POM to the MAOM fraction.

In addition, avoiding the use of mineral fertilizers and pesticides in BIODYN, which affect soil microbial community structure (Hartmann et al., 2015), also had no positive effect on OM stabilization in MAOM, compared to CONFYM.

Overall, the constant supply of OM through organic fertilizers in BIODYN and CONFYM initiates an improved aggregate stability and different sorption mechanisms of OM to fine mineral surfaces, compared to CONMIN and NOFERT. Therefore, our hypothesis that organic fertilization would lead to increased stabilization of MAOM, is true.

3.4.2. Dynamic stability of MAOM-C - highest contents despite highest turnover under organic fertilization

We expected higher MRTs and lower turnover of MAOM under organic fertilization, because of the supposedly higher stability of MAOM-C in BIODYN and CONFYM (i.e. enhanced aggregation, higher oxidation resistance (**Figure 3.2**)) compared to CONMIN and NOFERT. However, MRTs of MAOM were significantly higher in NOFERT (238 ± 40 yrs) and CONMIN (195 ± 27 yrs), compared to CONFYM (138 ± 18 yrs) and BIODYN (140 ± 19 yrs) (**Figure 3.4a**). These results were surprising given the fact that chemical oxidation with NaOCl has been shown to leave C with significantly higher ages and MRTs (Jagadamma et al., 2010; Kleber et al., 2005; Kögel-Knabner et al., 2008b). This shows that chemical methods are of limited use in differentiating the stability of OM to biodegradation (Mikutta and Kaiser, 2011).

In BIODYN and CONFYM, the increased microbial activity (Krause et al., 2022) ensured a faster processing of the steady high supply of young OM from organic fertilizers. This led to an increased accumulation of young microbial degradation products in MAOM, significantly shorter MRTs (-78 yrs) (**Figure 3.4a**) and significantly higher annual C mass flow rates in MAOM ($+70$ kg C ha⁻¹ yr⁻¹) (**Figure 3.4b**), compared to NOFERT and CONMIN. The amount of MAOM-C in BIODYN and CONFYM remained constant over

the 36-year period from 1982 to 2017 (**Figure 3.2** and **Table S3.4**). This implies that the faster turnover of MAOM-C in BIODYN and CONFYM (factor 1.7) is compensated by the even greater OM input rates (factor 2.3), resulting in higher MAOM-C contents, relative to NOFERT and CONMIN.

The omission of additional OM inputs via fertilization in NOFERT and CONMIN resulted in a high spatial substrate heterogeneity (Lehmann et al., 2020b; Shi et al., 2021), reducing the likeliness for the spatial co-occurrence of MAOM and decomposers (Don et al., 2013). The unchanged ^{14}C activity in MAOM during the steady-state period in NOFERT (2003-2017) (**Figure 3.3**) illustrates these low OM inputs of which very little was incorporated into MAOM over this period. As a result, a small, old OM fraction was isolated and preserved that turned over much slower, resulting in longer MRTs compared to CONFYM and BIODYN (**Figure 3.4a**). The fact that the older MAOM in NOFERT had significantly lower aromatic C than younger MAOM in BIODYN (Mayer et al., 2022a), supports the assumption that its reduced turnover and longer MRT resulted from the spatial isolation from its decomposers and not due to its recalcitrance to microbial degradation. This is in line with findings of Kleber et al. (2011), who showed that OM with the highest ^{14}C age (i.e. highest MRTs) had an easily metabolizable chemical composition.

We found no quantitative increase in MAOM-C of BIODYN and CONFYM over the 36-year period despite high OM inputs (**Table S3.1**). This underlines that direct management of MAOM-C is not possible. Using the empirical formulas of Hassink (1997) and Wiesmeier et al. (2015), Mayer et al. (2022a) showed high C saturation deficits of the fine fraction ($<20\ \mu\text{m}$) for all farming systems. Thus, C saturation is not an explanation for the lack of MAOM-C enrichment. Furthermore, the ^{14}C data of this study show the continuous rejuvenation of MAOM with new OM across all farming systems (**Figure 3.3**), contradicting that the 36-year period was too short for the incorporation of new OM in MAOM. Imaging techniques could provide further insight into the mechanistic processes that control and/or limit the accumulation of OM within MAOM at the submicron scale and improve our knowledge of how different fertilizer types might affect these processes (Steffens et al., 2017; Vogel et al., 2014).

Overall, we found MAOM-C to be more active in farming systems receiving organic fertilizers than in purely mineral and unfertilized systems, which was contrary to our hypothesis of longer MRTs in BIODYN and CONFYM. Just recently, attention has been drawn to the need for continuous turnover and microbial utilization of OM inputs to agricultural soils in order to maintain OM storage, aptly termed 'dynamic stability' by Dynarski et al. (2020). In our study, the 'dynamic stability' is manifested by the rapid and constant turnover of continuous OM inputs from composted (BIODYN) and stacked manure (CONFYM), and the subsequent stabilization of its degradation products in MAOM. This highlights the importance of maintaining continuous organic inputs in general, as a stop is anticipated to result in the fastest OM degradation in farming systems with high C turnover and short MRTs.

3.4.3. Clay content and clay mineralogy are crucial for OM stabilization - in the absence of organic fertilizers

We observed a strong positive correlation between clay content and the estimated MRT, especially in farming systems without organic fertilization (**Figure 3.5a**). This suggests that at low MAOM-C contents, clay content has greater influence on the stabilization (or 'retention') of OM than at higher MAOM-C contents. In the latter, OM sorption is less limited by vacant binding sites on mineral surfaces due to the preferable formation of organo-organos compounds (Possinger et al., 2020). Thus, the amount of clay particles is less critical for the stabilization of OM in CONFYM and BIODYN. In NOFERT and CONMIN, where MAOM-C contents are low, increased clay contents enhance the high spatial substrate heterogeneity (Lehmann et al., 2020b; Shi et al., 2021) (see *Chapter 3.4.2.*) via stabilization and physical isolation of OM in aggregates, further reducing substrate availability to microbes and, as a result increase MAOM MRT.

Furthermore, we observed a positive correlation between smectite content and estimated MRT (**Figure 3.5b**). Wattel-Koekkoek et al. (2003) identified clay mineralogy as the main factor explaining differences in MRT of OM, with the slowest turnover times in smectite-dominated soils. Smectite is an expendable 2:1 phyllosilicate with a high sorptive capacity due to its large SSA (Kleber et al., 2021; Saidy et al., 2013). The effect of smectite properties on MRT was stronger in NOFERT and CONMIN compared to CONFYM and BIODYN.

Notably, the outlier plots 88, 93, and 94 with the highest clay contents per farming system (**Table 3.1**), are directly adjacent in the DOK experimental design (**Figure S3.1**). This illustrates that at low SOM contents and in the absence of organic fertilization, even small clay content gradients at the field or plot level (NOFERT: 15-25%, CONMIN: 20-24%) (**Table 3.1**) can result in significant differences in MRT. For practice, this should raise awareness towards the fact that SOM turnover is also controlled by the heterogeneity of soil properties, particularly when OM inputs from fertilizers are missing. Consequently, exact knowledge about the heterogeneity of soil properties, e.g., through replicated and geolocated samplings, helps to minimize uncertainties in estimates of SOM persistence.

3.5. Conclusions

Using ^{14}C analysis and MRT estimation of the physically separated MAOM fraction ($<6.3\ \mu\text{m}$), we demonstrated that constant organic fertilization resulted in significantly higher MAOM-C turnover and significantly shorter MRTs compared to non-organic fertilization over a 36-year period. Despite the highest MAOM-C turnover, MAOM-C contents were kept constant under organic fertilization, implying that the faster turnover is compensated by the high OM input rates. The results of this study illustrate that a constant supply and turnover of OM in mineral-associated fractions is vital to ensure the long-term stability of MAOM-C contents. However, we lack understanding on the sub-micron scale mechanisms that control C sequestration in MAOM explaining the limited accumulation of additional MAOM-C. This will improve the evaluation of the ability of agricultural soils to act as long-term C sinks. Overall, this study highlights the importance of the dynamic nature of organo-mineral interactions for SOM stabilization, especially in the context of advancing climate change. Supporting this dynamic nature of SOM via continuous organic fertilization and improving biological soil quality should therefore become the focus of sustainable and climate-friendly agriculture. This corroborates the theory of managing SOM rather than locking it away, which mixed farming systems that integrate livestock and arable farming are best suited for.

CHAPTER 4:
GENERAL DISCUSSION AND
CONCLUSIONS

As a basis for the following discussion, **Figure 4.1** provides a comprehensive summary of the key findings from *Chapters 2* and *3*, focusing on the schematic representation of the farming system-driven mechanisms involved in SOM cycling.

Over the 36-year observation span in the DOK trial, the farming systems without fertilization (NOFERT) and solely mineral fertilization (CONMIN) exhibited significant losses of bulk SOC, whereas the application of organic manure resulted in the accumulation of bulk SOC (CONFYM and BIODYN). However, the observed increase in bulk SOC was limited to the highly labile and easily degradable oPOM fraction. Organic fertilization in CONFYM and BIODYN resulted in an increased microbial activity (Krause et al., 2022; Lori et al., 2023), facilitating the rapid turnover of the consistently high input of young POM (illustrated by the green gears in **Figure 4.1**). This increased the formation of aggregates and as a consequence oPOM accumulation (see also **Figure 2.3b**). In BIODYN, the farming system-specific composting of manure (i.e. qualitative manure differences) and the absence of pesticides led to the highest microbial activity, aggregate formation and oPOM-C contents (represented by the higher abundance of aggregates and microbial biomass compared to CONFYM in POM **Figure 4.1**). The increased POM-C turnover in CONFYM and BIODYN also led to an increased accumulation of young microbial transformation products and necromass in MAOM (illustrated by the thick green arrows in **Figure 4.1**), which is also expressed by the higher MAOM ^{14}C activity compared to NOFERT and CONMIN (see **Figure 3.3**). This led to a significantly higher MAOM-C turnover (see **Figure 3.4b**, illustrated by the grey gears in **Figure 4.1**) and shorter MRTs (see **Figure 3.4a**) compared to NOFERT and CONMIN.

It may sound paradoxical at first, but a constant supply of OM inputs and the subsequent rapid turnover of OM within the MAOM fraction is necessary to maintain its C content in the soil (i.e. concept of 'dynamic stability', see *Chapter 3*). In a broader sense, this principle can be visualized as an **engine and a fuel tank**. The application of organic fertilizers in CONFYM and BIODYN can be seen as fuel that is introduced into the soil, which is the fuel tank. The introduced OM undergoes rapid utilization by soil microbes, promoting increased microbial activity (i.e. combustion). Consequently, this microbial activity triggers the "activation" of the previously passive/less dynamic MAOM fraction (i.e. fuel reserve). The increased MAOM turnover rates and accompanied MAOM-C losses (i.e. fuel reserve consumption) (represented by the thick red arrows in **Figure 4.1**) are only offset by the high OM inputs, resulting in consistent MAOM-C contents from 1982 to 2017, but without any additional accumulation of MAOM-C. In other words, fuel replenishment and fuel reserve consumption balance each other out in CONFYM and BIODYN.

In NOFERT and CONMIN, OM input via fertilization is absent (i.e. no additional fuel input), and only OM through crop residues and root inputs is introduced into the soil. The consequently reduced microbial activity (represented by the green gears with fewer teeth in **Figure 4.1**), introduces a smaller amount of

young microbially processed OM into the MAOM (see **Figure 3.3**, illustrated by the small green arrows in **Figure 4.1**). This however stimulates turnover of MAOM-C, albeit less strongly than in CONFYM and BIODYN (represented by the smaller grey gears in **Figure 4.1**), resulting in significant MAOM-C losses (i.e. fuel reserve consumption) over the 36-year observation period (represented by the red arrows in NOFERT and CONMIN in **Figure 4.1**), due to insufficient fuel replenishment via organic fertilizer inputs.

In summary, the intricate interaction between POM and MAOM fractions, as depicted in **Figure 4.1**, demonstrates that soil C cannot be viewed as a singular entity. Consequently, its management requires a comprehensive systems-based approach, as just very recently advocated by Angst et al. (2023).

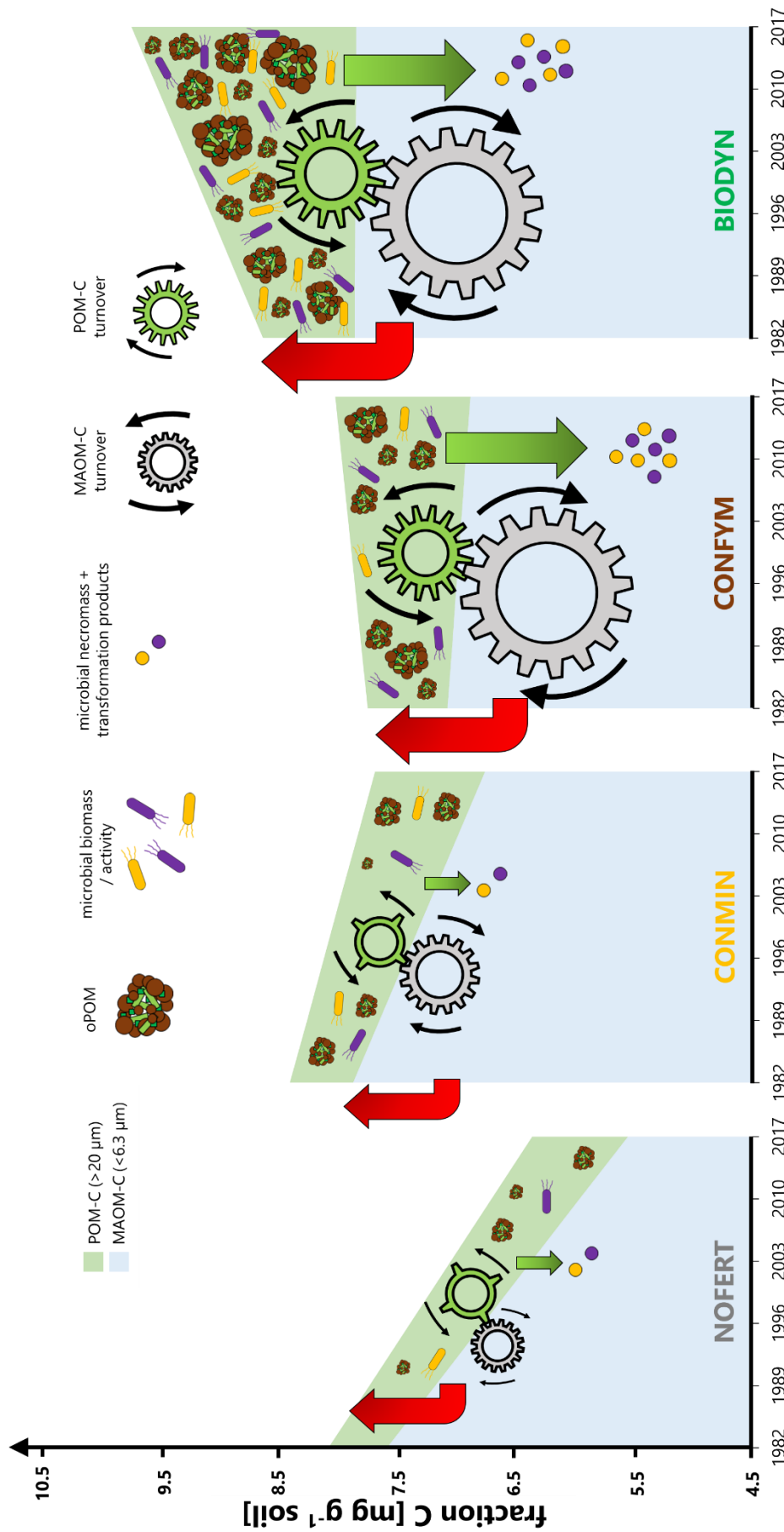


Figure 4.1. Schematic representation of farming system-induced impacts on POM- and MAOM-C turnover and the temporal evolution of the respective C contents within each of the four analyzed systems. On the x-axis, the observation period from 1982 to 2017 is shown. On the y-axis are the recovered fraction C contents, with light blue representing the MAOM-C (<6.3 μm) and green representing the POM-C contents (>20 μm). The grey and green gears represent the C-turnover in the MAOM and POM fraction, respectively. The green arrows indicate the input of microbial degradation products from the POM to the MAOM, and the red arrows indicate the loss of MAOM-C via turnover. Note: this graph is for illustrative purposes. The scaling of the y-axis does not start at zero, which serves to illustrate the POM-C fraction, which otherwise would be too small compared to the MAOM-C fraction. In addition, the illustrated fraction C contents do not reflect the actual measured data (see Table S2.3). Only the initial and final values (1982 and 2017) are measured values. The values in between were calculated based on the slope of the straight line between these two values.

4.1. Dampening the optimism - soil C sequestration under future climate

The lack of any additional C accumulation in the MAOM fraction (<6.3 μm) between 1982 and 2017, despite the low levels of C saturation (see **Figure 2.6**), calls into question the ability of agricultural soils to act as stable long-term C sinks and the effectiveness of soil management strategies to contribute to climate change mitigation. MAOM-C contents are only maintained by the constant supply and processing of organic fertilizers in CONFYM and BIODYN, dampening expectations for the highly touted C sequestration potential of agricultural soils. This highlights the fact, that direct targeted management of MAOM-C is insufficient, and underscores the significance of POM fractions as direct precursors of MAOM, with microorganisms acting as a pivotal regulatory factor.

The significance of these findings cannot be emphasized enough, especially in the light of the projected increase in global temperatures to 2.7°C by the end of the century (Lenton et al., 2023), which will profoundly affect SOC contents due to increased rates of OM decomposition (Conant et al., 2011; Smith et al., 2008). Extensive research on this issue, starting decades ago (e.g. Kirschbaum (1995), Schimel et al. (1990)) has contributed to a prevailing agreement within the scientific community regarding the adverse effects of increasing temperatures on the storage of C in soil. This consensus has been supported by the growing body of data-based evidence from modeling studies in recent years (e.g. Riggers et al. (2021), Wiesmeier et al. (2016), Meersmans et al. (2016)).

By analyzing more than 9000 globally distributed soil profiles, Hartley et al. (2021) showed substantial climate change induced C losses, especially in coarse-textured soils, leading to the assumption that unprotected C pools, such as the labile POM fractions are most affected by increasing temperatures (Knorr et al., 2005). This should be particularly critically viewed, as these fractions serve as precursors for stabilized MAOM and are the only additional C that accumulated over the long-term in the (partly) organically fertilized farming systems of the DOK trial (see **Figure 2.3b** & **4.1**). However, such losses could be offset by a corresponding increase of plant inputs to soil (Lugato et al., 2021). Recent findings from SOC stock models under different climate scenarios (RCP2.6, 4.5, 8.5) until 2099 for German croplands projected that excessively high amounts of organic inputs would be required (increases of 51% to 93% compared to current inputs), solely to compensate for previous SOC losses (Riggers et al., 2021). These excessive amounts would entail drastic changes in agricultural management, often rendering them uneconomic for farmers (Poulton et al., 2018), especially impractical for integrated and mixed farming systems that combine livestock and arable farming, such as CONFYM and BIODYN.

In addition it was shown that soil C responses to increasing temperatures are mainly a function of the intrinsic microbial temperature sensitivity within the soil (Walker et al., 2018). In a recent study, Chen et

al. (2023) demonstrated that increasing temperatures lead to the suppression of the microbial pathway responsible for the formation of stabilized soil C, i.e. the reduced production of microbial transformation products and necromass. This was suggested to be a major cause of stabilized C loss in surface soil, as increasing temperatures would at the same time stimulate the microbial utilization of MAOM-C (Chen et al., 2023). The extent of these losses of MAOM-C are possibly a function of the microbial C use efficiency (Allison et al., 2010). In the DOK trial, Fließbach et al. (2007) showed that microorganisms in BIODYN need less energy to maintain their biomass (i.e. reduced basal respiration in relation to microbial biomass), compared to microorganisms within CONFYM and CONMIN (20% and 52% more energy, respectively). Based on these findings, it can be inferred that the MAOM-C in BIODYN may be less susceptible to temperature-induced losses caused by climate change compared to the other analyzed farming systems. Consequently, despite overall low expectations, BIODYN emerges as the favorable management option for future considerations regarding long-term C sequestration.

Given the massive climate change-induced limitations on C sequestration in agricultural soils that have emerged from extensive research, it is necessary to review the feasibility of what is arguably the most prominent initiative ('4p1000' Minasny et al. (2017), see **Chapter 1.5**) to build SOC stocks for climate mitigation. As a reminder, this action plan aims at an annual increase of 4‰ or 0.4% in global SOC stocks (upper 30-40 cm) via sustainable management practices, which would largely offset anthropogenic CO₂ emissions and achieve food security. However, this initiative has recently come under some heavy criticism in the scientific community (e.g. "An idea that is politically brilliant does not necessarily make scientific or practical sense" (Baveye et al., 2018)). This criticism stems mainly from the discrepancy between the theoretically and technically achievable C storage potential and the extensive body of evidence from studies that supports it. In a recent study by Rodrigues et al. (2021), an assessment was conducted to determine the country-specific potential for C sequestration in croplands across 24 European countries. The result was rather sobering, as none of the evaluated countries' C sequestration potentials met the ambitious target set by the 4p1000 initiative. In another study, the projected C sequestration potential for Bavaria, Germany, through various C storage measures accounted for merely 30% of the intended objective (Wiesmeier et al., 2017). Additionally, in the case of France, achieving the target would require a 30-40% increase in C inputs to the soil over a 30-year period (Martin et al., 2021). Taking climate change into account, Bruni et al. (2021) projected, based on 14 long-term agricultural trials in Europe, that an increase of 54-120% in C inputs would be necessary.

In pursuit of what appears to be a rather elusive goal, how do the observed bulk SOC changes among the four analyzed DOK-farming systems, as depicted in **Figure 2.2**, perform with respect to achieving it? C stock changes from 1982 to 2017 were in the order NOFERT < CONMIN < CONFYM < BIODYN (**Table 4.1**). The 4p1000 Initiative's requirements for C sequestration were only met in the BIODYN system under

pure organic fertilizer application as composted manure. Here, over the 36-year period, C stocks increased at an annual rate of $0.41 \pm 0.40\% \text{ yr}^{-1}$, which was equal to $0.20 \pm 0.18 \text{ t C ha}^{-1} \text{ yr}^{-1}$. This, however, with high fluctuations between the plot replicates (high standard deviation) (**Table 4.1**) and only as labile oPOM, which is subject to loss within days to weeks (see **Figure 2.4a**).

Table 4.1: Calculated C stocks, C stock changes and corresponding CO₂ equivalents in the four analyzed DOK farming systems over the period from 1982 to 2017. C stocks were calculated using mean bulk densities from CRP1 for each plot, assuming that they remained stable (Leifeld et al., 2009).

farming system	C stock [t ha ⁻¹]		C stock change			CO ₂ equivalents	
	1982	2017	[t ha ⁻¹]	[t ha ⁻¹ yr ⁻¹]	[% yr ⁻¹]	[t ha ⁻¹]	[t ha ⁻¹ yr ⁻¹]
NOFERT	37.41 ± 4.08	29.96 ± 2.91	-7.46 ± 1.58	-0.21 ± 0.04	-0.69 ± 0.12	-27.34 ± 5.79	-0.76 ± 0.16
CONMIN	38.55 ± 4.59	35.67 ± 3.68	-2.88 ± 1.57	-0.08 ± 0.04	-0.22 ± 0.12	-10.56 ± 5.75	-0.29 ± 0.16
CONFYM	37.28 ± 3.26	39.13 ± 2.35	1.85 ± 2.57	0.05 ± 0.07	0.13 ± 0.19	6.80 ± 9.44	0.19 ± 0.26
BIODYN	39.29 ± 4.65	46.52 ± 5.83	7.23 ± 6.54	0.20 ± 0.18	0.41 ± 0.40	26.51 ± 23.99	0.74 ± 0.67

In light of the findings from the DOK trial and the aforementioned studies on the limited potential of C sequestration in agricultural soils, it is even more questionable why soils are still being publicly and media-effectively attributed a huge C storage potential. Just recently, **the Synthesis Report of the Intergovernmental Panel on Climate Change (IPCC) Sixth Assessment Report (AR6)** on climate change (IPCC, 2023) was finalized during the IPCC's 58th Panel Session in Switzerland. In it, agricultural soils are given a high potential in terms of C sequestration to mitigate climate change, with only solar and wind energy and the reduced conversion of natural ecosystems being attributed higher potentials. Especially given the expected climate-related impacts on soil C, this enthusiasm for soil C sequestration as a significant solution for climate change mitigation should be critically viewed.

Overall, the soil under BIODYN appears to have a supposedly measurable climate effect, compared to the other farming systems analyzed. However, there are considerable uncertainties surrounding this impact. Moreover, utilizing pure organic fertilization in the form of composted manure seems to better prepare the soil to handle future climate-related challenges. This could encourage a shift in mindset, moving away from soil management strategies for climate change mitigation towards management that enhances the soil's resilience against future climate impacts. These discussions are elaborated upon in **Chapter 4.2**. In general however, it is crucial to have realistic expectations for C sequestration in agriculture (Schlesinger and Amundson, 2018), and effectively communicate these to both the general public and practitioners. This enhances the credibility of the scientific community and, in turn, the trust that farmers have in it.

4.2. Implications for policy and future directions of soil management strategies

The attractiveness of offsetting one's own (e.g. companies) emissions (at least in part) through the climate-friendly measures of others has triggered a veritable boom in voluntary C markets in recent years, creating a lucrative business. However, to be eligible for C credits in recognition of farming practices aimed at C sequestration, specific criteria must be met (see **Chapter 1.5**). As C markets have experienced a surge in popularity, so have the number of soil C certification standards. This has led to the landscape of private C certificates being commonly described as a "jungle," owing to the intricate and diverse range of options and regulations (Demenois et al., 2022). Unfortunately, these private certificates often fail to meet expectations for climate change mitigation because they cannot guarantee the permanence of the created C sinks, one of the major criteria that has to be met (Paul et al., 2023). Moreover, achieving permanence in soil C sinks poses a significant challenge, particularly when targeted management of the MAOM-C fraction (i.e. stabilized C) is insufficient, even over extended periods (see **Figure 2.5b & 4.1**).

As shown in *Chapter 4.1*. (see *Table 4.1*), the increased bulk C stocks in BIODYN would have financially rewarded farmers in form of C credits. Considering that the observed increase in C stocks occurred solely in the highly labile oPOM fraction, which can be lost within a few days to weeks after harvest (see **Figure 2.4a**), the timing of soil sampling becomes a crucial factor for the allocation of C credits. If a farmer practices sustainable soil management, such as in the case of BIODYN, but is unable to sample the soil until several weeks after harvest due to various reasons, it is likely that C credits would not be awarded for that specific period. Conversely, if sampling is conducted in a timely manner the following year, the increase in C stocks would be measurable, and C credits could be allocated without any changes in management. Furthermore, it should be noted that if timely soil sampling had been conducted, it would not have been revealed that the observed increase in C was solely in labile form. This is because the current practice of assigning C credits does not differentiate between labile and stable C storage. This example is indicative of the current state of C certification, which appears to be more confusing than convincing for interested practitioners. Therefore, there are clear demands for uniformity of regulations and transparency (Oldfield et al., 2022). This would ensure integrity and bring clarity to practitioners, navigating through the complex landscape of certification standards.

Nonetheless, the accounting of **temporary C sinks** is currently an important point of scientific discussion in the field of C farming, as it was only recently shown that even short-term, i.e. **non-permanent soil C sinks** would have a quantifiable beneficial effect on climate mitigation (Leifeld, 2023; Leifeld and Keel,

2022). This perspective is gaining traction within the scientific community (Angst et al., 2023) and shows that the labile C stock increase in BIODYN does have a mitigation effect.

While economic and structural factors primarily emerge as the predominant factors influencing farmers' decision-making regarding the implementation of management practices (Bartkowski and Bartke, 2018), there is a tendency to overlook the influence of other factors, particularly social factors, on this process. This has the potential to hamper the effectiveness of environmental payment systems (Brown et al., 2021). Whether the implementation of sustainable agricultural management practices is driven by economic incentives is, however irrelevant for climate mitigation in the first place. Any measure aimed at preserving and building up SOM is to be considered laudable. However, it is essential to emphasize the need for ongoing and sustained efforts, as the cessation of C farming practices will result in the loss of C from the soil (see **Figure 1.7**), potentially even at faster rates than its initial buildup (Smith, 2005). If we look specifically at the development of SOC contents under the analyzed farming systems in the DOK trial, it is helpful to consider the previously introduced visualization of SOM dynamics as a running engine (**Figure 4.1**). Thus, it can be assumed that in BIODYN and CONFYM, where microbial activity is increased, i.e. all the gears are in motion (**Figure 4.1**), the cessation of management practices will not result in an abrupt halt, i.e. "brake at full speed". The engine will probably continue to run for a while even without the addition of organic fertilizers (i.e. fuel replenishment) (see *Chapter 3.4.2*). This, in turn, will possibly lead to the loss of MAOM-C (i.e. consumption of fuel reserves) due to lack of alternatives available to microbial degradation (Chen et al., 2023).

Furthermore, it was also observed, that the accrual of C is way more efficient in soils with low initial C saturation (Georgiou et al., 2022; Stewart et al., 2007), and is dominated by site-specific factors, such as soil texture (Rosinger et al., 2023). This can result in scenarios where a farmer, who may not have practiced sustainable soil management in the past, is rewarded C credits for achieving a rapid increase in soil C content after implementing a C farming measure. Conversely, a farmer who has consistently maintained the C content of his/her soil through sustainable practices, may not receive recognition due to the establishment of a new C flow equilibrium after a certain period of time (see **Figure 1.7**). The lack of fairness in this regard can lead to feelings of resentment among farmers.

In addition to financially rewarding C farming practices, it has been proposed to monetize the provision of essential soil functions (i.e. "natural capital") that are supported by continued sustainable management practices (Baveye et al., 2016). These functions include improved soil fertility, water retention capacity, enhanced soil structure, reduced risks of erosion and ultimately increased agricultural productivity for food security. Hence, it is reasonable to contemplate the establishment of, what I refer to as "**soil quality credits**" to recognize and incentivize sustainable management practices, independent of their direct climate benefits. Such an approach could prevent dedicated sustainable

farmers from being discouraged or demotivated. In this context, the issue of measuring or quantifying soil quality would undoubtedly gain significant attention (Bünemann et al., 2018; Dominati et al., 2010), presenting a distinct challenge in comparison to the measurement of C contents when allocating C credits.

Overall, the view that soil management should focus on maintaining soil quality and fertility, with C sequestration considered an additional or outcome, is gaining momentum in the scientific community (Moinet et al., 2023; Poulton et al., 2018; Powlson and Galdos, 2023), indicating a **paradigm shift**. Moinet et al. (2023) aptly put it in a nutshell: "Away from climate-smart soils, we need a shift towards soil-smart agriculture, adaptative and adapted to each local context". This aligns with the perspective of Berthelin et al. (2022), who emphasizes that farmers should prioritize enhancing soil C contents as a means of building resilience to climate change, rather than solely pursuing climate mitigation strategies. Nevertheless, it is crucial to recognize that any C sequestration, regardless of the scale, plays an important role in contributing to climate change mitigation, but should be viewed as a beneficial secondary outcome (Moinet et al., 2023).

4.3. Limitations

Examining the dynamics of SOM in LTEs presents a substantial scientific challenge, given the numerous factors that can potentially influence the outcomes over the course of the observation period. Moreover, the processing of samples during laboratory work can introduce additional methodological challenges. While this thesis primarily focused on the effects of fertilizer inputs on SOM dynamics, it is important to acknowledge that there are external variables that could have influenced the observed SOM dynamics in the DOK trial, which were not within the scope of our examination. Consequently, in this chapter, the potential impacts of these factors are elucidated, accompanied by a discussion on their potential influence on the outcomes obtained in this thesis. By considering these factors and reflecting on the observations made, we will address the possible limitations and provide recommendations for future research.

4.3.1. C loss during physical fractionation

The choice of fractionation method and its careful execution determine the accuracy of the C contents in the separated, functionally distinct fractions and thus the significance of the results in terms of SOM dynamics in the soil. When evaluating the performance of a fractionation method, it is crucial to take into account the C recovery and reproducibility (Poeplau et al., 2018). The mean **C recovery rate** after physical fractionation procedures was $72.7 \pm 4.4\%$ across all 96 samples analyzed in this thesis. This means that on average, approximately a quarter of the initial bulk SOC was lost during the physical fractionation process. This C loss poses a major issue since the exact source SOM fractions of these losses cannot be precisely determined. However, the recovery rates were very similar and showed no significant differences between farming systems (NOFERT: $71.3 \pm 4.0\%$; CONMIN: $72.4 \pm 4.8\%$; CONFYM: $72.8 \pm 3.4\%$; BIODYN: $74.2 \pm 4.9\%$) (**Figure 4.2a**) and analyzed years (1982: $74.3 \pm 4.9\%$; 1989: $74.1 \pm 5.1\%$; 1996: $74.1 \pm 5.1\%$; 2003: $70.2 \pm 3.3\%$; 2010: $71.1 \pm 3.3\%$; 2017: $72.3 \pm 4.7\%$) (**Figure 4.2b**). The consistency of C recoveries demonstrates the high reproducibility of the fractionation method, with methodologically caused C losses that were unaffected by the duration of the DOK trial and farming systems.

Since soil mass recovery after fractionation averaged approximately 95%, we assume that most of the C was lost as soluble C (Helbling et al., 2021), which is due to the use of the heavy liquid Na-polytungstate. In particular, the repeated and thorough rinsing of the fraction $<20 \mu\text{m}$ to remove Na-polytungstate prior to particle size fractionation (see **Figure S1.10**) likely resulted in the mobilization and subsequent loss of C (Plaza et al., 2019). Similar findings regarding the magnitude and source of C loss have been reported in other studies (Crow et al., 2007; Helbling et al., 2021; Just et al., 2021). Thus, assuming that

all of these constant C losses originate from the fine fractions $<20\ \mu\text{m}$ and therefore adding them to the recovered C amounts, the development of these fraction C contents within the farming systems does not change over the years, as well as when comparing between different farming systems. Nevertheless, it is important to note that the loss of C during fractionation always entails a loss of information. Therefore, we strongly recommend including the recovery rates alongside the results in publications to ensure transparency and to inform readers about potential limitations regarding the interpretation and significance of the findings. Unfortunately, numerous studies fail to do so, which underscores the importance of critically evaluating their validity.

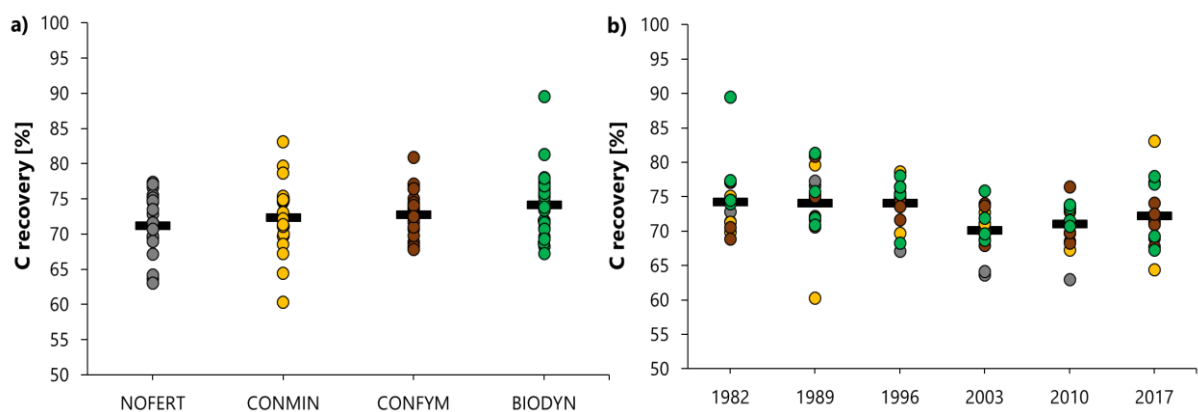


Figure 4.2: Comparison of C recovery rates after physical fractionation procedures **a)** between the analyzed farming systems and **b)** between the analyzed years. The black bars represent the mean of plot replicates and the circles show the single plot replicates, colored according to each farming system.

In addition, the use of Na-polytungstate represented by far the highest running costs and the rinsing process was very time consuming. We therefore recommend the use of fractionation schemes that avoid the use of heavy liquids, such as Na-polytungstate. Recently, it has been shown that the use of simplified fractionation approaches without the use of heavy liquids (i.e. no density fractionation) (Fuchs et al., 2023; Just et al., 2021) was sufficient with regards to the separation of fast ($>20\ \mu\text{m}$) and slow cycling ($<20\ \mu\text{m}$) SOM fractions. They also found a very high reproducibility, as well as mass and C recovery rates. However, the lack of a density fractionation step due to the omission of heavy liquids makes it impossible to distinguish between different POM fractions (i.e. fPOM and oPOM). If there is a desire to separate the POM and obtain insights into the impact of different fertilizers on the labile C protected within aggregates, I recommend to carry out the density fractionation step independently using Na-polytungstate. In this case, refer to steps 1-5 in **S1.1** for detailed instructions on how to perform this process.

4.3.2. The role of mineral fertilizers in nutrient supply and SOM formation

The emphasis of this thesis primarily revolved around examining the impact of farming systems on soil C contents. However, in light of the dilemma outlined in *Chapter 1.1*, concerning the challenge of simultaneously mitigating climate change AND ensuring food security, the discussion regarding **plant nutrition** and its role in supporting **crop productivity** under the farming systems in the DOK trial was not sufficiently dealt with in *Chapters 2* and *3*. Furthermore, the potential **impacts of mineral fertilization on soil C contents** were not explicitly addressed. These aspects will be briefly discussed in the following section.

In a global meta-analysis, Knapp and van der Heijden (2018) discovered that organically managed soils exhibited a notably lower temporal yield stability, which refers to the reliability of crop production over successive years, compared to conventionally managed soils. This difference was primarily attributed to the intensified utilization of mineral fertilizers and consequently higher availability of nutrients for crops in conventional farming practices. It is crucial to critically assess this aspect, particularly within the context of food security amidst the anticipated impacts of climate change and rising global temperatures.

In the DOK trial, the total nutrient input during CRP2-6 was 26% and 35% lower in BIODYN, compared to CONMIN and CONFYM, respectively (**Table S2.2**). This resulted in significantly more plant-available nutrients for direct crop uptake in CONMIN and CONFYM due to the input of mineral fertilizers. Accordingly, crop yields are on average about 15-20% higher in CONMIN and CONFYM, compared to BIODYN (Mäder et al., 2002; Mayer et al., submitted).

To facilitate plant growth, it is essential for the nutrients contained in OM inputs to be released through microbial transformation, especially when relying on purely organic fertilizers, as in BIODYN. However, a challenge in this process arises from the stoichiometric imbalance between the microbial requirements and the elemental composition of OM from organic fertilizers. By introducing additional nutrients into the soil via mineral fertilization, stoichiometric imbalances between microbial needs and OM elemental composition may be alleviated (Manzoni et al., 2012), which may have further improved plant nutrition in CONFYM, compared to BIODYN. However, compost application has been observed to increase nutrient supply to crops (Reimer et al., 2023). Furthermore, pure organic fertilization with composted manure, significantly increased microbial activity in BIODYN, which led to the "activation" of the MAOM-C fraction (i.e. significantly higher turnover and shorter MRTs, see **Figure 4.1** & **Figure 3.4**). This led to a higher availability of MAOM-C, which could be utilized by microorganisms, resulting in the release of nutrients that were then accessible for plant uptake. This mechanism, involving the often overlooked role of MAOM as an important source for bioavailable N (Jilling et al., 2018), could to some extent compensate for the absence of mineral fertilizers, when compared to CONMIN and CONFYM. These

processes may have contributed to a slight narrowing of the yield gap between BIODYN and conventional systems.

In CONMIN, mineral fertilization provided increased plant input to the soil through increased primary production (Xu et al., 2021), which resulted in higher oPOM-C and MAOM-C contents compared to NOFERT (**Figure 2.3b** & **2.5b**). However, this was far from compensating for the lack of OM input via organic fertilizers compared to CONFYM and BIODYN. Microbial growth and respiration and therefore the transformation of OM inputs through microbial activity and subsequent incorporation into stabilized SOM pools, are also strongly influenced by the availability of nutrients in the soil (Kirkby et al., 2013; Kirkby et al., 2014; Mooshammer et al., 2014; Richardson et al., 2014). However, in CONFYM, the higher OM inputs combined with mineral fertilization did not result in increased C levels compared to BIODYN, likely due to the higher levels of labile C in CONFYM stacked manure compared to BIODYN compost. Furthermore, the long-term application of mineral fertilizers has been observed to decrease the contribution of microbial residues in POM and MAOM fractions (Zou et al., 2023). In addition, numerous studies have documented that the application of inorganic P to soil results in an increase of C loss via priming mechanisms (e.g. Fisk et al. (2015), Spohn and Schleuss (2019), Mehnaz et al. (2019)).

Finally, in the context of crop production and food security, it is important to consider the often overlooked aspect of energy expenditure associated with plant nutrition. With increased C contents, such as in BIODYN, the soil itself is likely to supply more nutrients to crops via microbial activities, which in turn reduces the reliance on mineral fertilizer inputs and energy consumption as well as GHG emissions associated with mineral fertilizer production (Powlson and Galdos, 2023). In the DOK trial, this was expressed as 40-50% lower energy expenditure in BIODYN, and considering the only 20% lower crop yields, crop production in BIODYN is more energy-efficient and sustainable compared to CONFYM and CONMIN (Mäder et al., 2002).

4.3.3. Soil depth and root C inputs

The majority of studies examining soil C dynamics tend to focus solely on topsoil layers (Yost and Hartemink, 2020). This is attributed to the higher SOM contents found in these layers, which are directly influenced by soil management practices (i.e. plow horizon). However, more than half of the global soil C is located in soil layers deeper than 30 cm (Balesdent et al., 2018; Jobbagy and Jackson, 2000), but C dynamics within these layers remains poorly understood (Rumpel and Kögel-Knabner, 2011).

Just recently, Skadell et al. (2023) showed that approximately 20% of soil management effects on soil C occur in a depth of 30-50 cm. The input of OM into deeper soil layers is mainly facilitated via root biomass and dissolved OM (Rumpel and Kögel-Knabner, 2011) and poses the primary source of C inputs

into the soil (Sokol et al., 2019). The literature presents divergent outcomes regarding the impact of these inputs on different SOM fractions. Rhizodeposition has been associated with a high MAOM formation efficiency (Villarino et al., 2021), and root exudates have been linked to a greater potential for destabilizing highly stabilized MAOM through priming effects (Bernal et al., 2016). In addition, root C inputs have been found as a way to actively control MRTs of SOM (Poeplau et al., 2021). To date there have been limited investigations into root biomass within the DOK trial (Hirte et al., 2018a; Hirte et al., 2018b). However, these studies have revealed yield-independent belowground C inputs and have shown comparable total root biomass and rhizodeposition between organic and conventional farming systems under wheat cultivation. Notably, when maize was grown, the organic system demonstrated elevated levels of rhizodeposition in comparison to the conventional system. This finding provides compelling grounds to further explore this direction in future investigations.

Only limited research exists on the effects of different fertilizer inputs on C in deep soil layers, and the findings of existing studies often yield inconsistent results. This emphasizes the need to “dig deeper” (Gross and Harrison, 2019) and follow the suggestion of Skadell et al. (2023), ensuring that soil samples are taken up to a depth of 50 cm, to fully capture the impacts of management practices on soil C. In the DOK trial, this would expand the understanding of SOM dynamics and might shed light onto how and to what extent the fertilizer inputs in different farming systems impact C in deeper soil layers.

4.3.4. N₂O emissions

Another significant factor to consider, particularly regarding the climate impact of farming systems, is the emission of N₂O, a main contributor of total agricultural greenhouse gas GHG emissions (Reay et al., 2012; Tubiello et al., 2015). However, this issue was not covered in this thesis. The main sources of agricultural N₂O emissions come from mineral N fertilizers and organic manures, which accounts for the major part of the agricultural share of approximately 65% of global N₂O emissions (Tian et al., 2019). Considering the growing global food demand, a subsequent increase in N₂O emissions can be anticipated in the future. Just recently, Guenet et al. (2021) and Lugato et al. (2018) showed that disregarding N₂O emissions undermines the validity of statements regarding the climate impact of soil C management measures. This is because the potential climate mitigation effect of additional C storage is often offset by N₂O emissions and might even increase with additional C. In the light of these findings, it seems questionable, if the soil C increase in BIODYN has any positive climate effect, as claimed earlier (see **Chapter 4.1 & 4.2**). This adds another discouraging setback to the notion of combatting climate change through increased C inputs to soils and underscores the need to shift away from this strategy (see **Chapter 4.2**).

4.4. Conclusions and outlook

In summary, the findings of this study emphasize the need to reassessing soil management strategies with regards to C storage, as revealed through a comprehensive analysis of SOM dynamics in the DOK system comparison trial. Even after adopting sustainable organic soil management practices for 36 years, there was no measurable additional accumulation of MAOM-C, which is the SOM fraction responsible for long-term C sequestration and climate mitigation. Furthermore, this thesis has shown that the MAOM, believed to be passive, is much more active than previously thought, which is facilitated by the application of organic fertilizers. Therefore, the long-standing "carbon dilemma" already raised by Janzen (2006), regarding whether we should utilize or preserve soil C, can now be answered in favor of utilization. This represents a paradigm shift that has already gained recognition in the scientific community in recent years (Moinet et al., 2023; Poulton et al., 2018; Powlson and Galdos, 2023).

Nonetheless, any effort to increase the amount of SOM is commendable because of the resulting increase in soil fertility and the ability of soils to provide ecosystem services. In doing so, the results of this thesis break a lance for organic farming and join the multitude of studies showing the effectiveness of sustainable organic soil management in maintaining and accumulating additional SOM. Overall, the findings of this thesis showed that BIODYN, in addition to maintaining soil fertility, appears to have a measurable climate effect, compared to the other farming systems analyzed. However, there are considerable uncertainties surrounding this impact. Moreover, utilizing pure organic fertilization in the form of composted manure seems to better prepare the soil to handle future climate-related challenges.

The next crucial step is to collaborate with policymakers and, ultimately, the farmers who play a pivotal role in implementing these changes. As the final link in the implementation chain, their participation is essential. In this regard, it is important to remain credible as scientific community, provide clarity, and communicate realistic and achievable goals based on comprehensive research. Furthermore, moving forward from the results of this thesis, the use of the NanoSIMS technology, which was already introduced in **Chapter 1.3**, could provide help in deciphering stabilization mechanisms at the sub-micrometer level and therefore provide further important insights into SOM cycling.

Through this thesis, I aimed to contribute to the resolution of uncertainties surrounding the sustainable utilization of the invaluable resource of soil, particularly under the aspect of future climate-related impacts. In closing, I echo the fitting words of Davies (2017), which encapsulate the significance of this endeavor: "Soil is a common good and an essential resource. With the support of science, governments, civil society and businesses must ensure that it is not treated like dirt."

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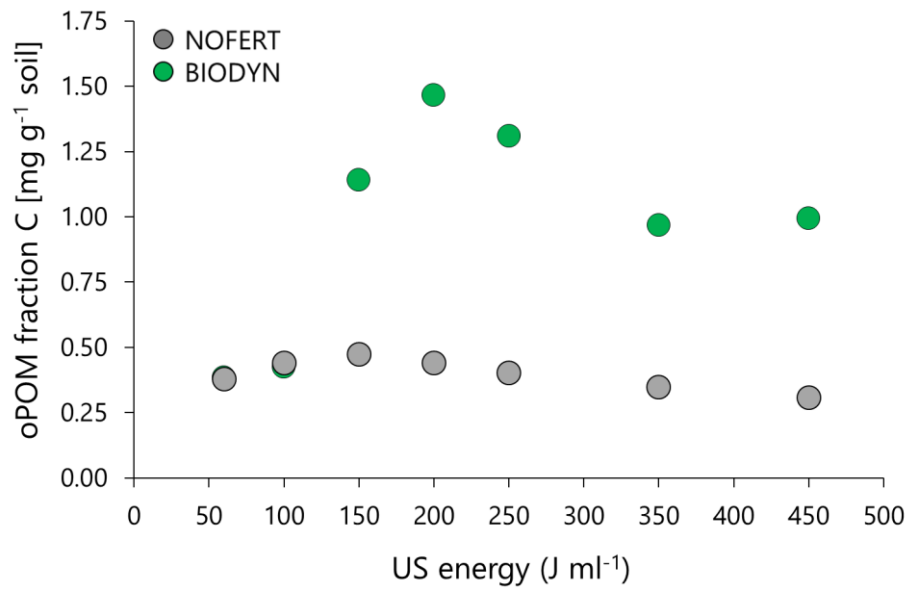
Supplementary Material - LABORATORY

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S1.1: Physical fractionation laboratory method developed at the FiBL soil physics laboratory

Note: the quantities/volumes of lab equipment and material given in this method description refer to the preparation and completion of the density fractionation procedure of **six soil samples per day at full workload**.

1.) Preparation of the density solution (Na-polytungstate)

Safety precautions: safety goggles, rubber gloves, protective clothing, under fume hood

Material: large spoon, Na-polytungstate (powder, low C and N content), 1 l plastic beaker with handle, tall measuring beaker, bar magnet, magnetic stirrer, hydrometer, 2 l Schott bottle



Figure S1.2: Laboratory equipment required for the preparation of the density solution.

Steps: (990 g Na-polytungstate = 1 l density solution) **(2x)**

It is important to choose Na-polytungstate powders with low C and N contents, otherwise this might lead to contamination of the samples (Kramer et al., 2009)

- dissolve 990 g Na-polytungstate in approx. 500 ml distilled water and stir well with a large spoon until the salt is completely dissolved
- pour the solution into the tall measuring beaker and add a bar magnet
- place the measuring beaker on a magnetic stirrer and let it run until the entire water column is mixed from top to bottom (help with spoon)
- let the hydrometer sink into the solution and gradually add distilled water until a density of **1.8 g cm⁻³** (yields 1 l of solution, i.e. enough for four samples)
- pour the solution into the Schott bottle
- repeat these processes until the volume of density solution is sufficient to fractionate six (or eight) samples in a "batch"

2.) Adding density solution to the soil sample

Safety precautions: safety goggles, rubber gloves

Material: soil samples (6), crystallizing glass dishes (6), Na-polytungstate solution (6 x 250 ml), 20 ml scintillation bottles (12), spoon, scale, tweezers, aluminum foil, measuring beaker, pasteur pipette

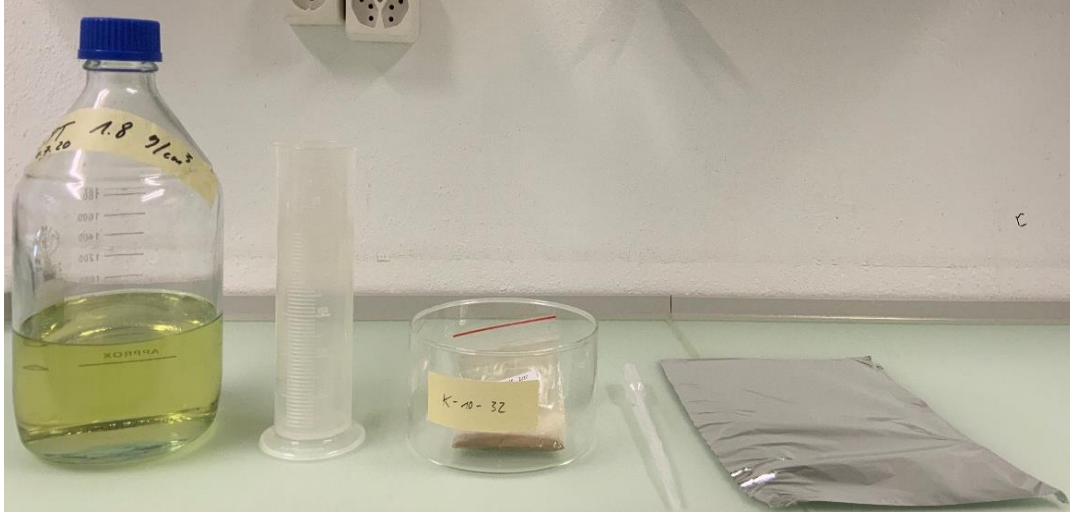


Figure S1.3: Laboratory equipment required for adding density solution to soil samples.

Steps: (6x)

- for each of the six randomly picked bulk soil samples (air-dried, <2 mm), label one crystallizing dish ("sample name - bulk soil") and 2 scintillation bottles ("sample name - fPOM", "sample name - oPOM")
- per sample, weigh in 30 g (representative) of soil into the crystallizing dish and distribute the sample over the entire bottom of the dish by gentle shaking
- remove with tweezers all larger fPOM fragments and put them into the scintillation bottles labeled "fPOM"
- pour 250 ml of density solution into the measuring beaker. Then carefully add the solution over the side wall of the dish to the sample with the pasteur pipette until saturation (**Figure S1.4**)
- pour the remaining solution slowly over the edge of the dish (cause as little turbulence as possible to avoid bursting of aggregates and oPOM release)
- gently shake the dish to expose covered fPOM
- cover the dishes with aluminum foil and leave overnight



Figure S1.4: Fractionation steps for adding density solution to the soil sample

3.) Separation of free particulate organic matter (fPOM)

Safety precautions: safety goggles, rubber gloves

Material: vacuum pump + hose, suction flask + plug, 20 μm sieve (100 mm \varnothing), 1l glass beakers (2), conductivity meter, scintillation bottle, pasteur pipette, crystallizing dishes



Figure S1.5: Laboratory equipment required for aspiration and rinsing of fPOM from bulk soil.

Steps: (6x)

- gently shake the dish to remove fragments stuck to the side walls
- aspirate all fPOM with the vacuum pump into the suction flask (and as much solution as possible) → **do not aspirate mineral particles!**
- check the hose for stuck fPOM
- place the sieve on glass beaker and pour the suction flask content onto the sieve (set aside the glass beaker with the solution that passed the sieve)
- place the sieve on the other glass beaker and rinse remaining fPOM from the suction flask with distilled water onto it
- rinse fPOM on the sieve with distilled water until a conductivity of $<10 \mu\text{S cm}^{-1}$
- rinse fPOM with distilled water from the sieve into the scintillation bottle labelled "*sample name - fPOM*"
- put it in the freezer and set aside the glass beaker with the aspirated solution
- freeze-dry all fPOM samples



Figure S1.6: Fractionation steps for aspiration and rinsing of fPOM from bulk soil.

4.) Ultrasonication

Safety precautions: safety goggles, earplugs if necessary

Material: ultrasonic homogenizer, 600 ml glass beaker, lab scissor jack, crystallizing dish, ice, scraper, 1l glass beaker with aspirated solution, pasteur pipette, thermometer



Figure S1.7: Laboratory equipment required for ultrasonication of the mineral soil.

Steps: (6x)

- attach new crystallizing dish to the scissor jack with adhesive tape
- transfer the mineral soil fraction from the initial crystallizing dish with a scraper into a 600 ml glass beaker (rinse with aspirated solution from set aside 1l beaker)
- pour the remaining solution into the 600 ml beaker
- place the beaker in the new dish and fill the dish with water, then with ice
- place all in the ultrasound box and immerse the sonotrode 2.5 cm (for complete turbation)
- set the sonication duration and amplitude (60%) as determined during pre-tests (see **Figure S.1.1**) according to Griepentrog and Schmidt (2013) and start sonication
- during sonication, keep track of the temperature of the solution (<30 °C) to prevent alteration of SOM quality and align the beaker so that the sonotrode is always centered

4.1.) Calibration and maintenance of the ultrasonic homogenizer

- due to deterioration of the sonotrode tip (see right side in **Figure S1.8**), regular calorimetric calibrations of the ultrasonic homogenizer should be performed

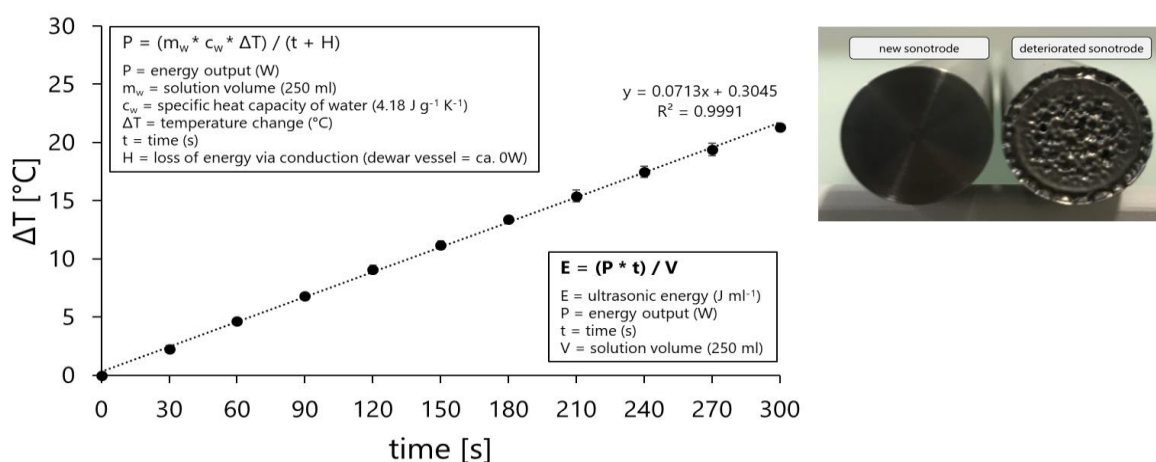


Figure S1.8: Calorimetric calibration of the ultrasonic homogenizer. Black circles show mean values of temperature change within the solution that resulted in a constant energy output of 75 W during all the conducted fractionation runs in this study.

5.) Separation of occluded particulate organic matter (oPOM)

Safety precautions: safety goggles, rubber gloves

Material: 250 ml centrifuge bottles (12x), funnel, spray bottle, vacuum pump, hose, suction flask + plug, 20 μm sieve (100 mm \varnothing), 1l glass beaker

Steps: (6x)

- evenly transfer the sonicated solution and mineral soil into two 250 ml centrifuge bottles with a funnel (accurate to 1 g), label lid and bottle
- centrifuge: place the bottles of the same sample opposite each other. Set timer to 15 min and speed to 7000 rpm. Start the centrifuge
- aspirate the floating oPOM and as much of the solution as possible into the suction flask
→ **do not aspirate mineral particles!**
- set aside the centrifuge bottles with the remaining mineral soil
- place the sieve on the 1 l glass beaker and pour the aspirated oPOM and solution onto the sieve
- rinse oPOM on the sieve with distilled water until a conductivity of $<10 \mu\text{S cm}$
- rinse oPOM with distilled water from the sieve into the scintillation bottle labelled "*sample name - oPOM*" and put it in the freezer
- freeze-dry all oPOM samples

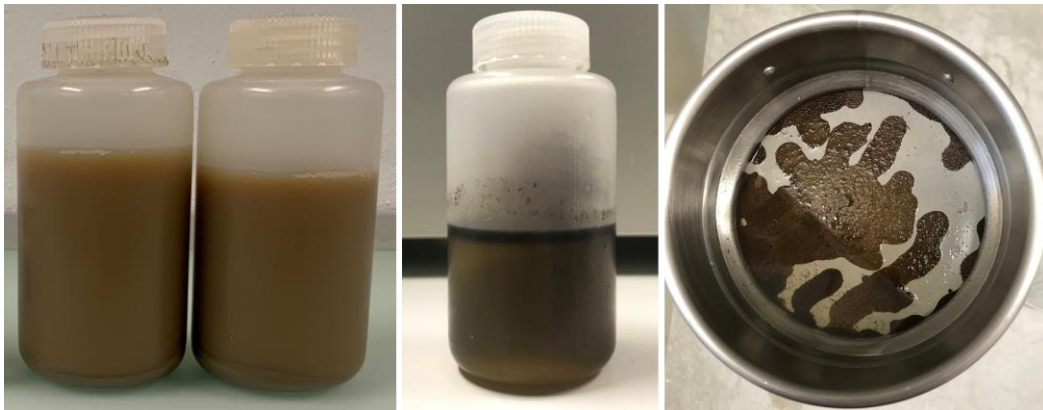


Figure S1.9: Fractionation steps for aspiration and rinsing of oPOM from bulk soil.

6.) Rinsing of the remaining mineral fraction

Safety precautions: safety goggles

Material: scale, wide-neck bottles (6), vacuum pump, hose, suction flask + plug, centrifuge beakers, spray bottle

Steps: (6x)

- take the set aside centrifuge bottles with the remaining mineral soil and fill them with distilled water (accurate to 1 g)
- place the bottles in the centrifuge (opposite to each other) and start centrifuging (15 min, 7000 rpm)
- aspirate the water with the vacuum pump, measure conductivity, refill the bottles with distilled water and thoroughly shake the bottles
- repeat until a conductivity of $<50 \mu\text{S cm}^{-1}$ (takes up to eight runs, see **Figure S1.10**)
- transfer the rinsed mineral fraction into a labelled wide-neck bottle and refrigerate

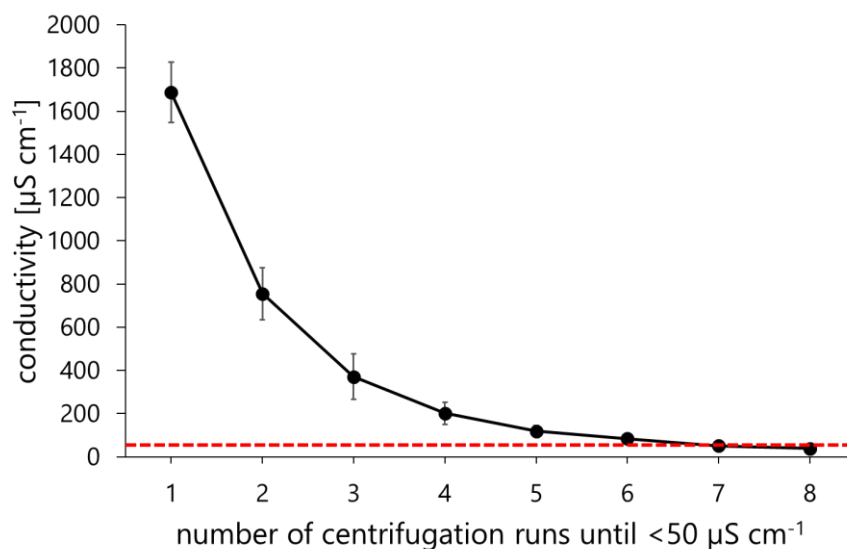


Figure S1.10: Development of electrical conductivity of the remaining mineral fraction after repeated centrifugation and rinsing. The black circles show mean values of 30 fractionated bulk samples with standard deviations. The dotted red line is the threshold of $50 \mu\text{S cm}^{-1}$, after which centrifugation was stopped.

7.) Fractionation of the remaining mineral soil

Safety precautions: -

Material: vibrating sieve tower (630, 63 and 20 μm sieves, 200 mm \varnothing), wide-neck bottles, spray bottle, funnels, 5 l beaker with handle, hose and water supply, tweezers

Steps: (6x)

- place the outlet tray with the hose discharging into the 5 l beaker at the bottom of the sieve tower, followed by the 20, 63, 630 μm sieves (the 630 μm sieve was additionally used to avoid clogging of the sieves)
- pour the rinsed mineral fraction from the wide-neck bottle onto the 630 μm sieve
- mount the dome with the water nozzles on top. Start and gently adjust the flow of water and the vibration setting of the tower
- try to keep the water volume as low as possible (important for further particle size fractionation of the fraction $<20 \mu\text{m}$)
- as soon as the water discharge from the outlet tray is clear, stop sieving
- clean the sieves (tweezers) and rinse the material on the 630 and 63 μm sieves, and on the 20 μm sieve into a labelled beakers ("*sample name - 2000-63 μm* ", "*sample name - 63-20 μm* ")
- fill the discharge from the 5 l beaker into labelled wide-neck bottles ("*sample name - $<20 \mu\text{m}$* ")



Figure S1.11: Wet-sieving of the mineral fraction after separation of POM fractions.

- the remaining particle size fractionation included the separation via sedimentation in Atterberg-cylinders into the fractions 20-6.3 and $<6.3 \mu\text{m}$ at the Institute of Geological Sciences, University of Bern.



Figure S1.12: Particle size fractionation of the mineral fraction $<20 \mu\text{m}$ via sedimentation.

- all separated mineral fractions were dried at 60°C , grinded and measured for C and N

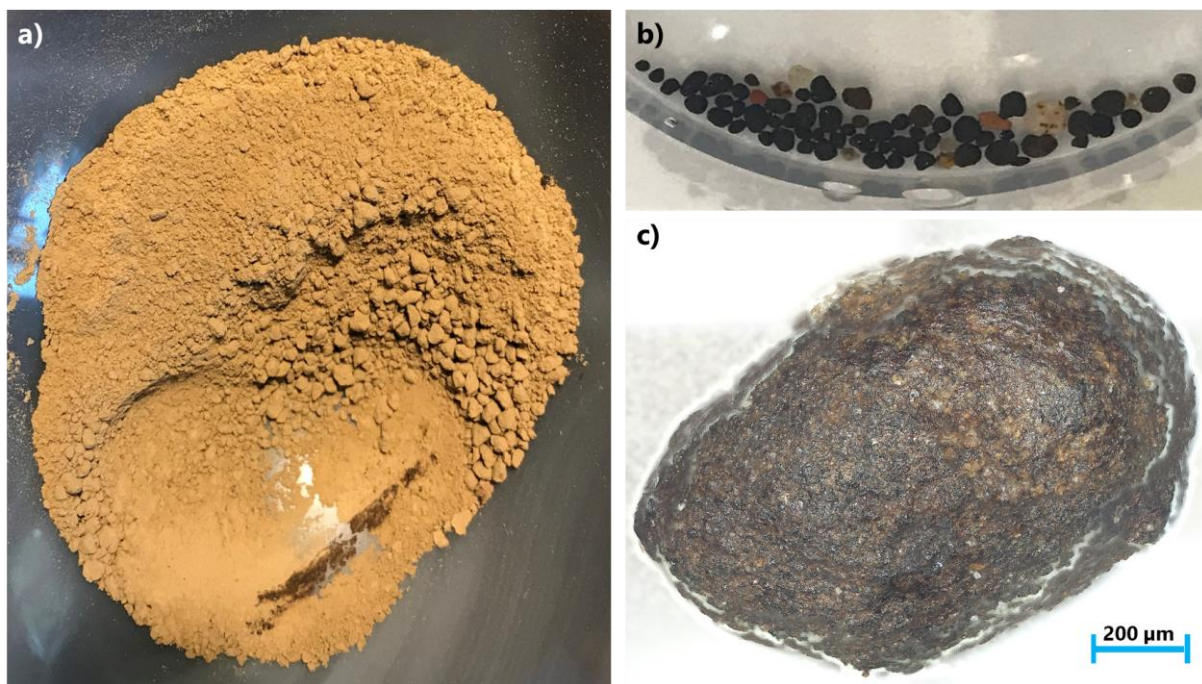


Figure S1.13: **a)** During grinding of the bulk samples for elemental analysis (C and N measurements), blackish-brown streaks repeatedly occurred which were strongly distinguishable in color from the rest of the sample. **b)** During density fractionation, small black, rounded beads were found that caused the dark coloration during grinding. **c)** By observation under the microscope, these were identified as manganese concretions.



Figure S1.14: Soil profile of the Haplic Luvisol in the DOK experiment. The blackish-brown smears, which are the result of working the profile with a spade, show iron-manganese concretions. See also **Figure S1.13**. Photo: Markus Steffens.

Supplementary Material - CHAPTER 2

Table S2.1: Composition of the first six completed crop rotation periods (CRP) corresponding to the temporal shift for subplot B in the DOK trial (adapted from Krause et al. (2022)). Crops present on the plots during years of analysis (5th year each CRP) are highlighted in bold.

	CRP 1 (1978-1984) 1982	CRP 2 (1985-1991) 1989	CRP 3 (1992-1998) 1996	CRP 4 (1999-2005) 2003	CRP 5 (2006-2012) 2010	CRP 6 (2013-2019) 2017
1 st	Winter wheat 2	Winter wheat 2	Winter wheat 2	Winter wheat 2	Winter wheat 2	Winter wheat 2
2 nd	Barley	Barley	Grass-clover 1	Grass-clover 1	Grass-clover 1	Grass-clover 1
3 rd	Grass-clover 1	Grass-clover 1	Grass-clover 2	Grass-clover 2	Grass-clover 2	Grass-clover 2
4 th	Grass-clover 2	Grass-clover 2	Grass-clover 3	Potato	Silage corn	Silage corn Green manure
5 th	Potato Green manure	Potato Green manure	Potato	Winter wheat 1 Green manure	Winter wheat 1 Green manure	Soybean
6 th	Winter wheat 1 <i>Intercropping</i>	Winter wheat 1 <i>Intercropping</i>	Winter wheat 1 <i>Intercropping</i>	Soybean <i>Green manure</i>	Soybean <i>Green manure</i>	Winter wheat 1 <i>Intercropping</i>
7 th	White cabbage	Beetroot	Beetroot	Silage corn	Potato	Potato

Table S2.2: Mean annual nutrient inputs from the 2nd to 6th crop rotation period (CRP) [kg ha⁻¹ yr⁻¹] and annual inputs relative to CONFYM [%] (adapted from Krause et al. (2022)) across all subplots in the DOK trial. N_{tot} refers to total nitrogen inputs. N_{min} is the sum of NH_4^+ -N and NO_3^- -N from slurry or mineral fertilizers. P refers to phosphorous and K refers to potassium. OM refers to organic matter inputs. CN ratios of OM inputs were calculated as $(OM / 1.72) / (N_{tot} - N_{min})$.

	N_{tot}		N_{min}		P		K		OM		CN ratio
	[kg ha ⁻¹ yr ⁻¹]	[%]	[kg ha ⁻¹ yr ⁻¹]	[%]	[kg ha ⁻¹ yr ⁻¹]	[%]	[kg ha ⁻¹ yr ⁻¹]	[%]	[kg ha ⁻¹ yr ⁻¹]	[%]	
NOFERT	-	-	-	-	-	-	-	-	-	-	-
CONMIN	121	71	121	107	38	103	246	99	-	-	-
CONFYM	171	100	113	100	37	100	248	100	2314	100	23
BIODYN	93	54	26	23	24	65	179	72	1911	83	17

Table S2.3: Recovered SOC (mg g^{-1} soil) after physical fractionation in POM and MAOM fractions for each treatment and year of analysis. Arithmetic means are highlighted in bold with standard deviations of $n = 4$ replicates. Post-hoc Tukey letters give significant differences at $p < 0.05$.

	year & crop rotation period (CRP)					
	1982 (CRP 1)	1989 (CRP 2)	1996 (CRP 3)	2003 (CRP 4)	2010 (CRP 5)	2017 (CRP 6)
fPOM-C (>20 μm) [mg g^{-1}]						
NOFERT	0.16 ± 0.04 a	0.23 ± 0.06 a	0.33 ± 0.11 a	0.31 ± 0.06 a	0.26 ± 0.05 a	0.33 ± 0.07 a
CONMIN	0.21 ± 0.04 ab	0.28 ± 0.10 ab	0.39 ± 0.14 a	0.43 ± 0.11 a	0.26 ± 0.08 a	0.35 ± 0.05 a
CONFYM	0.28 ± 0.09 b	0.29 ± 0.10 ab	0.38 ± 0.07 a	0.33 ± 0.05 a	0.27 ± 0.07 a	0.44 ± 0.07 a
BIODYN	0.31 ± 0.05 b	0.36 ± 0.07 b	0.31 ± 0.06 a	0.61 ± 0.06 b	0.40 ± 0.16 a	0.47 ± 0.26 a
oPOM-C (>20 μm) [mg g^{-1}]						
NOFERT	0.33 ± 0.05 a	0.35 ± 0.32 a	0.29 ± 0.04 a	0.19 ± 0.05 a	0.18 ± 0.04 a	0.47 ± 0.11 a
CONMIN	0.33 ± 0.06 a	0.49 ± 0.12 a	0.34 ± 0.06 a	0.34 ± 0.25 a	0.31 ± 0.07 a	0.58 ± 0.07 a
CONFYM	0.39 ± 0.03 ab	0.80 ± 0.23 ab	0.27 ± 0.06 a	0.43 ± 0.15 a	0.18 ± 0.05 a	0.70 ± 0.08 a
BIODYN	0.46 ± 0.09 b	1.13 ± 0.10 b	0.56 ± 0.08 b	0.96 ± 0.28 b	0.50 ± 0.12 b	1.42 ± 0.16 b
sand-sized (2000-63 μm) OM-C [mg g^{-1}]						
NOFERT	0.14 ± 0.04 a	0.25 ± 0.11 a	0.11 ± 0.03 a	0.18 ± 0.05 a	0.13 ± 0.04 ab	0.24 ± 0.06 a
CONMIN	0.14 ± 0.03 a	0.18 ± 0.08 a	0.21 ± 0.19 a	0.16 ± 0.10 a	0.09 ± 0.04 a	0.19 ± 0.05 a
CONFYM	0.19 ± 0.06 a	0.16 ± 0.04 a	0.13 ± 0.04 a	0.12 ± 0.02 a	0.16 ± 0.02 b	0.24 ± 0.04 a
BIODYN	0.17 ± 0.06 a	0.28 ± 0.16 a	0.14 ± 0.03 a	0.32 ± 0.22 a	0.16 ± 0.05 b	0.22 ± 0.06 a
silt-sized (63-6.3 μm) OM-C [mg g^{-1}]						
NOFERT	2.03 ± 0.46 a	1.91 ± 0.07 a	2.04 ± 0.64 a	1.65 ± 0.19 a	1.45 ± 0.21 a	1.55 ± 0.20 a
CONMIN	2.12 ± 0.43 a	1.84 ± 0.34 a	2.32 ± 1.06 a	2.06 ± 0.11 ab	1.93 ± 0.19 ab	1.92 ± 0.23 ab
CONFYM	2.26 ± 0.30 a	1.82 ± 0.34 a	2.16 ± 0.44 a	2.08 ± 0.21 ab	2.22 ± 0.34 b	2.15 ± 0.07 ab
BIODYN	2.66 ± 0.72 a	2.07 ± 0.68 a	2.60 ± 0.50 a	2.68 ± 0.73 b	2.81 ± 0.26 c	2.53 ± 0.61 b
clay-sized (<6.3 μm) MAOM-C [mg g^{-1}]						
NOFERT	7.57 ± 1.15 a	6.78 ± 1.11 a	6.50 ± 1.43 a	5.45 ± 0.46 a	5.58 ± 0.71 a	5.55 ± 0.58 a
CONMIN	7.86 ± 1.34 a	6.69 ± 1.06 a	7.27 ± 1.73 a	6.37 ± 1.30 ab	6.55 ± 0.92 a	6.75 ± 0.81 ab
CONFYM	7.07 ± 0.83 a	6.88 ± 0.50 a	7.35 ± 0.76 a	6.45 ± 0.50 ab	6.92 ± 0.45 ab	6.88 ± 0.44 ab
BIODYN	8.34 ± 1.69 a	7.88 ± 1.38 a	8.86 ± 1.20 a	7.83 ± 1.10 b	8.42 ± 0.91 b	8.32 ± 1.26 b

Table S2.4: Current C contents (C_{cur}) (<20 μm) (calculated with fraction-C concentrations obtained from physical fractionation and fraction mass proportions determined by texture analysis (PARIO)) and C sequestration potential (C_{pot}) according to the empirical formula of Hassink (1997) and adjustments made by Wiesmeier et al. (2015). C saturation (C_{sat}) is calculated as the percentage of C_{cur} from C_{pot} . The C saturation deficit (C_{def}) is calculated as $C_{pot} - C_{cur}$. Arithmetic means are highlighted in bold with standard deviations of $n = 4$ replicates.

farming system	C_{cur} [mg g^{-1}]		C_{pot} [mg g^{-1}]		C_{sat} [%]		C_{def} [mg g^{-1}]					
	1982	2017	Hassink	Wiesmeier	Hassink	Wiesmeier	Hassink	Wiesmeier				
fine fraction												
<20 μm (%)	1982	2017	Hassink	Wiesmeier	Hassink	Wiesmeier	Hassink	Wiesmeier				
NOFERT	12.2 \pm 1.6	9.0 \pm 0.8	24.7 \pm 2.5	19.8 \pm 2.5	49.4 \pm 5.7	36.4 \pm 1.9	61.5 \pm 7.3	45.4 \pm 2.8	12.5 \pm 2.1	15.7 \pm 1.9	7.6 \pm 2.1	10.8 \pm 1.8
CONMIN	13.4 \pm 1.4	11.5 \pm 0.7	25.2 \pm 1.0	20.3 \pm 0.9	53.1 \pm 5.5	45.7 \pm 2.8	65.9 \pm 6.8	56.8 \pm 3.7	11.8 \pm 1.5	13.7 \pm 1.1	6.9 \pm 1.4	8.8 \pm 1.0
CONFYM	12.2 \pm 0.8	11.3 \pm 0.7	24.1 \pm 1.3	19.2 \pm 1.2	50.9 \pm 5.6	46.9 \pm 2.7	63.6 \pm 7.8	58.9 \pm 3.8	11.9 \pm 1.9	12.8 \pm 1.1	7.0 \pm 1.9	7.9 \pm 1.1
BIODYN	14.2 \pm 2.0	14.0 \pm 1.9	25.9 \pm 2.1	21.0 \pm 2.0	55.0 \pm 7.2	53.9 \pm 6.4	67.8 \pm 9.1	66.6 \pm 8.0	11.7 \pm 2.1	11.9 \pm 1.9	6.8 \pm 2.1	7.0 \pm 1.9

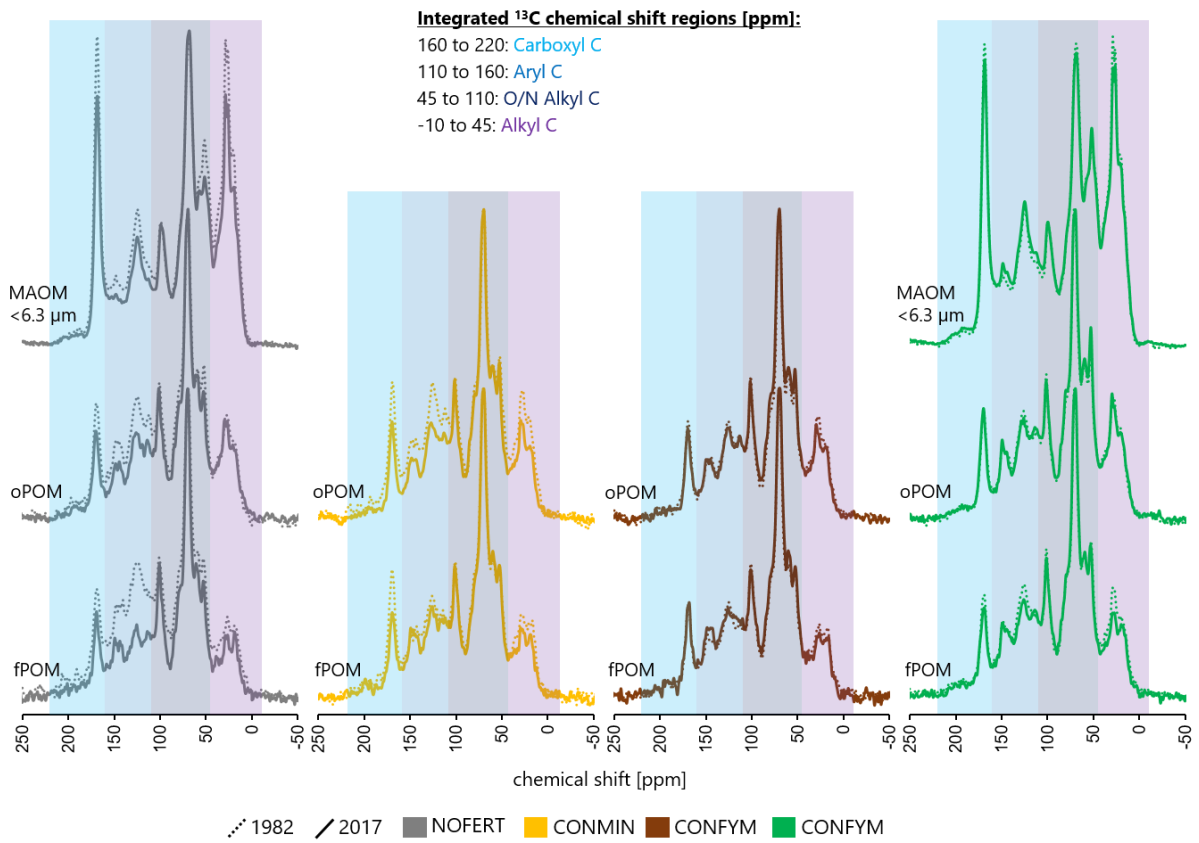


Figure S2.1: Solid-state ¹³C CPMAS-NMR spectra of selected POM and MAOM fractions. Dotted lines represent spectra from 1982 and solid lines from 2017. Segments highlighted in color represent the different corresponding integrated chemical shift area.

Supplementary Material - CHAPTER 3

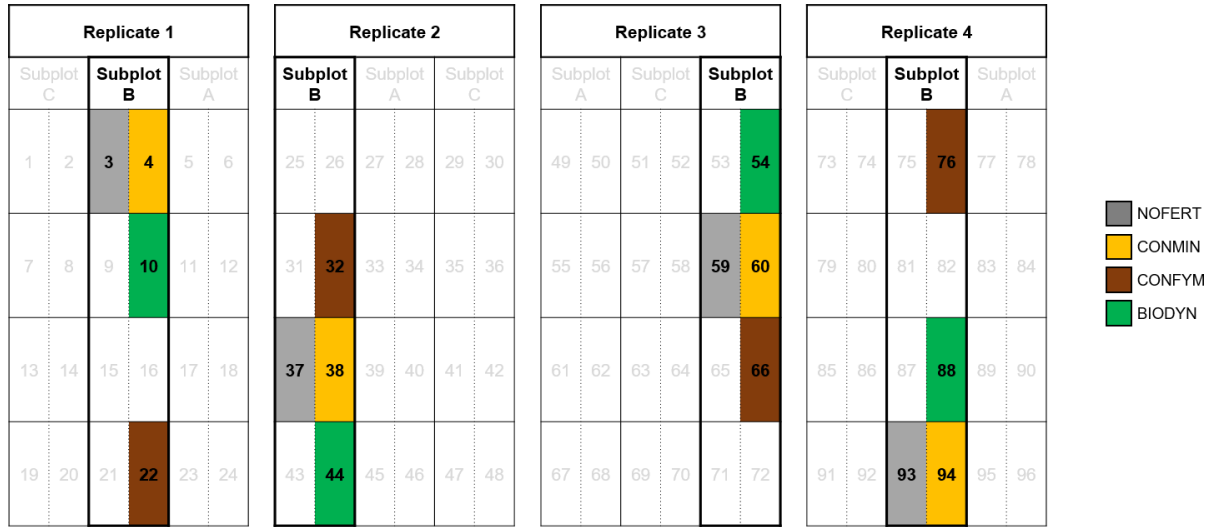


Figure S3.1: Field map of the DOK long-term experiment. The analyzed subplot B is framed in bold and the analyzed plots are color-coded according to the respective farming system.

Table S3.1: Recovered MAOM-C [mg g^{-1}] ($<6.3 \mu\text{m}$; 0-20 cm) after physical fractionation for each farming system and year of analysis. Values are arithmetic means with standard deviations of $n = 4$ replicates. Post-hoc Tukey letters give significant differences at $p < 0.05$. For a detailed overview including all separated fractions, see Table S2.3.

	MAOM-C [mg g^{-1}]					
	1982	1989	1996	2003	2010	2017
NOFERT	7.57 ± 1.15 a	6.78 ± 1.11 a	6.50 ± 1.43 a	5.45 ± 0.46 a	5.58 ± 0.71 a	5.55 ± 0.58 a
CONMIN	7.86 ± 1.34 a	6.69 ± 1.06 a	7.27 ± 1.73 a	6.37 ± 1.30 ab	6.55 ± 0.92 a	6.75 ± 0.81 ab
CONFYM	7.07 ± 0.83 a	6.88 ± 0.50 a	7.35 ± 0.76 a	6.45 ± 0.50 ab	6.92 ± 0.45 ab	6.88 ± 0.44 ab
BIODYN	8.34 ± 1.69 a	7.88 ± 1.38 a	8.86 ± 1.20 a	7.83 ± 1.10 b	8.42 ± 0.91 b	8.32 ± 1.26 b

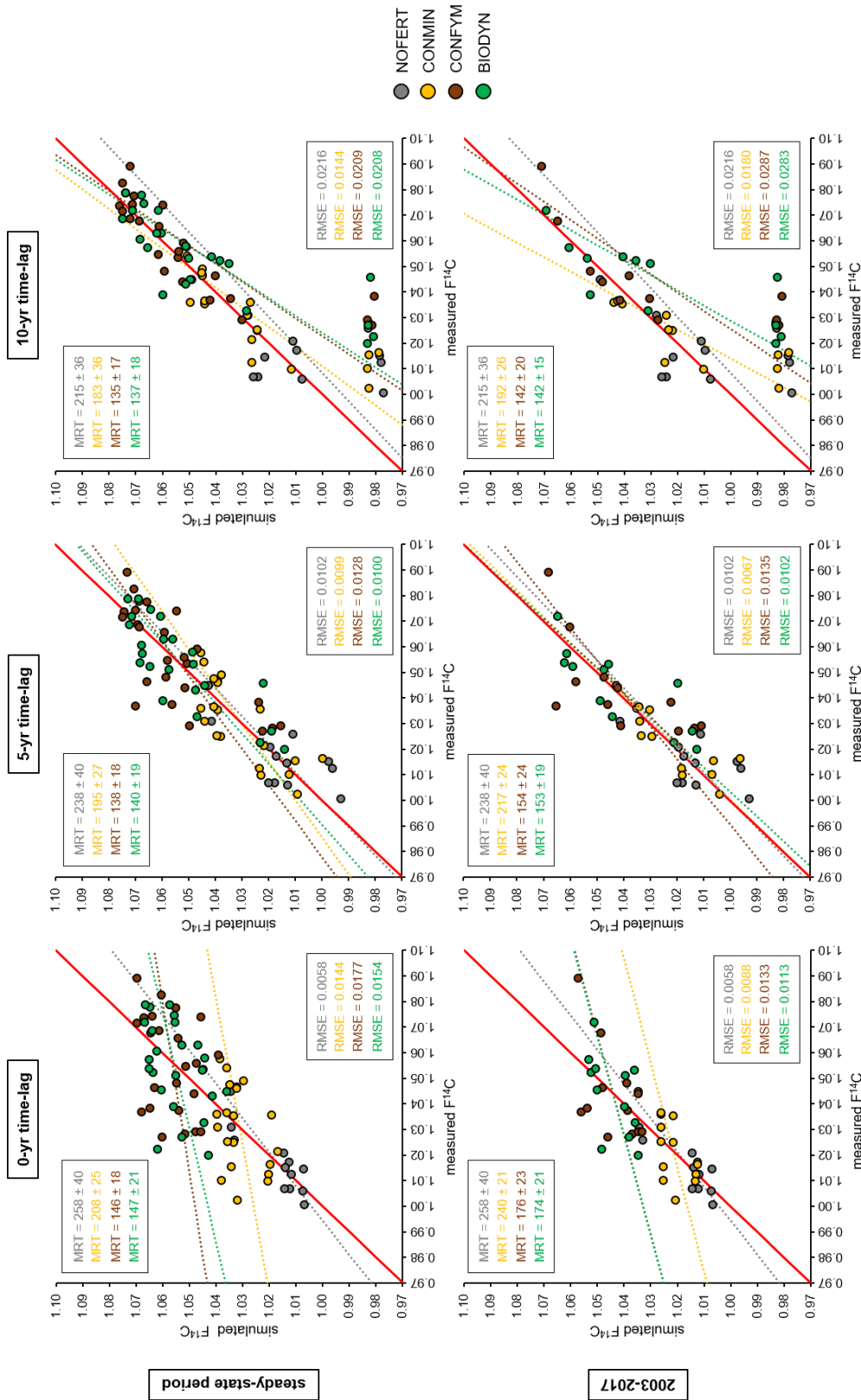


Figure S3.2: Comparison of measured and simulated ¹⁴C activity (in Fraction Modern, F¹⁴C) in MAOM (after Harkness et al. (1986)). Assumption of a 0-, 5-, and 10-year time lag (column 1, 2 and 3, respectively) between C assimilation by the crop and its storage in MAOM for the period during which this fraction of each farming system was in steady-state (NOFERT: 2003-2017, CONMIN: 1989-2017, CONFYM: 1982-2017, BIODYN: 1982-2017) (upper row) and the period during which NOFERT was in steady-state (2003-2017). The circles and dotted linear trends colored corresponding to the farming system show the deviation from the red line, which reflects the perfect fit between measured and modeled values. Root-mean-square errors (RMSE) of each farming system compared to the perfect prediction by the model and estimated mean residence times (MRT) are shown in the boxes.

Table S3.2: Comparison of measured and simulated ¹⁴C activity (in Fraction Modern, F¹⁴C) in MAOM during the steady-state period of each farming system (NOFERT: 2003-2017, CONMIN: 1989-2017, CONFYM: 1982-2017, BIODYN: 1982-2017) using the approach of Harkness et al. (1986). The measured ¹⁴C activity was corrected for radioactive decay between sampling and measurement year. For each analyzed plot at each tested time lag (0, 5 and 10 years between C assimilation of the crop and its incorporation in MAOM), the root-mean-square error (RMSE) and mean residence time (MRT) is shown. Values in bold represent the mean RMSE per farming system for each time lag. Values for CONFYM and BIODYN are shown on the next page.

farming system	plot	year	0-yr time lag				5-yr time lag			10-yr time lag			
			measured ¹⁴ C activity [F ¹⁴ C]	simulated ¹⁴ C activity [F ¹⁴ C]	RMSE	MRT [yrs]	simulated ¹⁴ C activity [F ¹⁴ C]	RMSE	MRT [yrs]	simulated ¹⁴ C activity [F ¹⁴ C]	RMSE	MRT [yrs]	
NOFERT	3	2003	1.0069	1.0122	0.0041	273	1.0178	0.0114	254	1.0242	0.0227	232	
		2010	1.0171	1.0124			1.0173			1.0097			
		2017	1.0126	1.0118			0.9961			0.9780			
	37	2003	1.0449	1.0346	0.0076	201	1.0426	0.0106	180	1.0491	0.0249	162	
		2010	1.0308	1.0344			1.0413			1.0279			
		2017	1.0258	1.0331			1.0110			0.9829			
	59	2003	1.0068	1.0143	0.0058	265	1.0200	0.0128	246	1.0259	0.0245	226	
		2010	1.0209	1.0145			1.0194			1.0110			
		2017	1.0152	1.0139			0.9975			0.9786			
	93	2003	1.0145	1.0071	0.0057	294	1.0132	0.0059	271	1.0216	0.0141	241	
		2010	1.0061	1.0073			1.0128			1.0076			
		2017	1.0005	1.0068			0.9929			0.9772			
						0.0058	258±40			0.0102	238±40		
	CONMIN	4	1989	1.0489	1.0298	0.0174	204	1.0376	0.0091	188	1.0449	0.0099	174
			1996	1.0468	1.0324			1.0391			1.0451		
2003			1.0355	1.0334			1.0391			1.0441			
2010			1.0250	1.0333			1.0379			1.0245			
2017			1.0025	1.0321			1.0091			0.9825			
38		1989	1.0542	1.0360	0.0176	187	1.0442	0.0101	173	1.0509	0.0141	161	
		1996	1.0576	1.0387			1.0455			1.0509			
		2003	1.0360	1.0397			1.0454			1.0496			
		2010	1.0309	1.0394			1.0440			1.0283			
		2017	1.0102	1.0379			1.0125			0.9830			
60		1989	1.0462	1.0322	0.0128	197	1.0392	0.0083	185	1.0451	0.0152	174	
		1996	1.0477	1.0348			1.0406			1.0453			
		2003	1.0365	1.0359			1.0406			1.0443			
		2010	1.0253	1.0357			1.0394			1.0246			
		2017	1.0155	1.0343			1.0099			0.9826			
94		1989	1.0215	1.0168	0.0098	244	1.0216	0.0120	234	1.0265	0.0185	224	
		1996	1.0358	1.0192			1.0231			1.0270			
		2003	1.0125	1.0204			1.0234			1.0266			
		2010	1.0099	1.0205			1.0228			1.0116			
		2017	1.0164	1.0197			0.9998			0.9788			
					0.0144	208±25			0.0099	195±27			

farming system	plot	year	0-yr time lag			5-yr time lag			10-yr time lag			
			measured ¹⁴ C activity [F ¹⁴ C]	simulated ¹⁴ C activity [F ¹⁴ C]	RMSE	MRT [yrs]	simulated ¹⁴ C activity [F ¹⁴ C]	RMSE	MRT [yrs]	simulated ¹⁴ C activity [F ¹⁴ C]	RMSE	MRT [yrs]
CONFYM	22	1982	1.0739	1.0455	0.0174	153	1.0546	0.0128	145	1.0599	0.0202	141
		1989	1.0548	1.0515			1.0581			1.0615		
		1996	1.0657	1.0542			1.0592			1.0612		
		2003	1.0482	1.0549			1.0585			1.0593		
		2010	1.0375	1.0540			1.0563			1.0346		
		2017	1.0282	1.0517			1.0185			0.9828		
	32	1982	1.0774	1.0551	0.0184	135	1.0657	0.0096	127	1.0707	0.0191	124
		1989	1.0687	1.0614			1.0692			1.0721		
		1996	1.0744	1.0641			1.0700			1.0712		
		2003	1.0678	1.0644			1.0687			1.0686		
		2010	1.0464	1.0630			1.0658			1.0402		
		2017	1.0271	1.0601			1.0224			0.9813		
	66	1982	1.0592	1.0390	0.0141	167	1.0470	0.0118	159	1.0523	0.0193	155
		1989	1.0534	1.0447			1.0505			1.0540		
		1996	1.0559	1.0474			1.0517			1.0540		
		2003	1.0441	1.0483			1.0513			1.0525		
		2010	1.0291	1.0476			1.0496			1.0302		
		2017	1.0290	1.0457			1.0154			0.9830		
	76	1982	1.0826	1.0606	0.0208	127	1.0707	0.0169	120	1.0750	0.0250	118
		1989	1.0738	1.0670			1.0742			1.0762		
		1996	1.0717	1.0696			1.0747			1.0751		
2003		1.0892	1.0697	1.0731			1.0722					
2010		1.0368	1.0680	1.0699			1.0422					
2017		1.0383	1.0647	1.0238			0.9804					
			0.0177	146±18				0.0128	138±18			
BIODYN	10	1982	1.0747	1.0558	0.0126	134	1.0643	0.0133	129	1.0670	0.0275	127
		1989	1.0607	1.0621			1.0678			1.0684		
		1996	1.0779	1.0647			1.0686			1.0678		
		2003	1.0574	1.0651			1.0674			1.0655		
		2010	1.0522	1.0636			1.0647			1.0383		
		2017	1.0456	1.0606			1.0219			0.9820		
	44	1982	1.0788	1.0575	0.0198	127	1.0688	0.0078	122	1.0738	0.0182	119
		1989	1.0685	1.0638			1.0723			1.0750		
		1996	1.0788	1.0664			1.0730			1.0740		
		2003	1.0718	1.0667			1.0715			1.0712		
		2010	1.0538	1.0652			1.0684			1.0416		
		2017	1.0224	1.0621			1.0233			0.9807		
	54	1982	1.0631	1.0467	0.0164	151	1.0559	0.0111	142	1.0605	0.0215	140
		1989	1.0631	1.0527			1.0594			1.0621		
		1996	1.0719	1.0554			1.0605			1.0617		
		2003	1.0389	1.0561			1.0597			1.0598		
		2010	1.0510	1.0551			1.0575			1.0349		
		2017	1.0271	1.0527			1.0191			0.9827		
	88	1982	1.0449	1.0359	0.0130	174	1.0440	0.0078	166	1.0495	0.0159	160
		1989	1.0432	1.0414			1.0474			1.0513		
		1996	1.0578	1.0441			1.0487			1.0514		
2003		1.0531	1.0450	1.0484			1.0501					
2010		1.0326	1.0445	1.0469			1.0286					
2017		1.0198	1.0428	1.0140			0.9830					
			0.0154	147±21				0.0100	140±19			

Declaration of consent

on the basis of Article 18 of the PromR Phil.-nat. 19

Name/First Name: Mayer / Marius Thomas

Registration Number: 11-065-737

Study program: PhD in Climate Sciences

Bachelor Master Dissertation

Title of the thesis: Sustainable management of organic matter in a Swiss arable soil - carbon sequestration dynamics under various farming systems

Supervisor: PD Dr. rer. nat. Markus Steffens

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