Rahul Datta
Ram Swaroop Meena *Editors*

Soil Carbon Stabilization to Mitigate Climate Change

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Biochar Role in Soil Carbon Stabilization and Crop Productivity

Jitka Prichystalova, Jiri Holatko, Tereza Hammerschmiedt, Rahul Datta, Ram Swaroop Meena, Marek Sudoma, Lucie Bielska, Maja Radziemska, Zygmunt Mariusz Gusiatin, Antonin Kintl, Meenakshi Sharma, Subhan Danish, Muhammad Zafar-ul-Hye, and Martin Brtnicky

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Abstract

In the presented chapter, various aspects related to carbon stabilization and storage in the form of biochar (an important soil amendment) are discussed. The following questions were considered: (i) what is the current general knowledge on biochar and its physicochemical composition, (ii) how manufacturing conditions affect biochar characteristics, including their role in carbon stabilization, (iii) how biochar contributes to soil carbon balance and storage, (iv) what are the effects of biochar on water retention in soil, soil erosion, production yields and economic productivity in agriculture, (iv) what are the effects of biochar on soil microbial community and activity, and (v) how biochar affects other soil amendments and their roles in soil. The present studies assess scientific outcomes and results which conclude that soil organic matter gained by organic residues can be used to enhance soil carbon storage. Following the published scientific results, the biochar amendment appears to be a promising way for increasing the stocks of recalcitrant carbon in the soil from a long-term perspective. Future research should focus on the designing, production, and use of enriched biochar, e.g. with nutrients, minerals, or microorganisms, to improve soil physicochemical properties, supply nutrients, and prevent their leaching. The fertilizer supplies accessible nutrients available to plants, and biochar can sequester depleted elements and prevent leaching of the added ones.

Keywords

Biochar · Carbon · Fertilizer · Soil amendment · Carbon sequestration

Abbreviations

AEC	Anion Exchange Capacity
AMF	Arbuscular Mycorrhizal Fungi
BC	Biochar
CEC	Cation Exchange Capacity
FT-ICR-MS	Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
GHG	Greenhouse Gas
IBI	International Biochar Initiative
LOC	Labile Organic Carbon
NMR	Nuclear Magnetic Resonance
Nr	Nutrients
OM	Organic Matter
R_{50}	Recalcitrance Index
SEM	Scanning Electron Microscopy
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
SPAC	Stable Polycyclic Aromatic Carbon
TOC	Total Organic Carbon

1 Introduction

Biochar (BC) is produced during high-temperature (300–800 °C) combustion of biomass under oxygen-limited conditions (i.e. pyrolysis), and therefore it contains a high proportion of stable carbon (Singh et al. 2012). Although a broad spectrum of biochar definitions exist in the literature, all of them concern conditions of biochar production and its characterization. For example, biochar is defined as solid carbonaceous residue, produced under oxygen-free or oxygen-limited conditions at temperatures ranging from 300 to 1000 °C (Saifullah et al. 2018) or as a carbon-rich product that has a high proportion of aromatic C and high chemical and biological stability (Li et al. 2017). If applied to the soil, it is thought to improve soil fertility and mitigate climate change due to its potential for storing anthropogenic carbon dioxide (CO_2) (Lehmann et al. 2011; Seifritz 1993). The annual capacity to sequester carbon in the form of thermally stabilized (charred) biomass (considering the utilization of all existing organic sources) applied to soil was estimated to be 1 Gt per year (Sohi et al. 2010). BC is not only produced artificially but can also be found in soils located in humid tropics, especially in Amazonia, as a result of ancient human activities and/or fires. These soils are referred to as Amazonian dark earth or Terra preta (Taketani et al. 2013). Unlike other tropical soils, they contain high levels of nitrogen, carbon, calcium, potassium, magnesium, phosphorus, and stable organic matter (Glaser et al. 2001). According to Gaskin et al. (2008), these nutrients are easily extractable and may be available for plants, which contributes to the high fertility of these soils. On the other hand, other authors stated that biochar could not be considered as a primary supply of nutrients. However, biochar is an adsorption matrix and may enrich the soil with several beneficial elements and minerals, which are the main perspective to improve the condition of the soil (Glaser et al. 2002; Lehmann et al. 2003a; Meena et al. 2018; Shenbagavalli and Mahimairaja 2012b).

2 Role of Biochar in Soil Carbon Stabilization

Despite the substantial topic, the processes of carbon stabilization have not been fully uncovered, and it is affected by many factors (Wiesmeier et al. 2019; Yang et al. 2020). Mechanisms to stabilize carbon stock include physical interactions, such as the reaction of soil mineral matrix with carbon compounds forming bonds inaccessible for decomposers; rigid chemical structure of some carbon substances, such as biochar, some humic acids or lipids; or by biological protection given by formation of micro-aggregates bound by hyphae or by some changes to residues within organisms intestine (Goh 2004).

Understanding of carbon stabilization is pivotal to improve agricultural management to store soil organic matter, soil structure, or to mitigate the greenhouse effect (Singh et al. 2018). Carbon stabilization is tightly related to carbon sequestration, which is the transformation of atmospheric carbon dioxide into soil carbon (Liao et al. 2020). Increased stabilization of sequestered carbon may help to mitigate the greenhouse effect (Goh 2004; Singh et al. 2018).

Biochar content can be roughly divided into leachable carbon, ash, and recalcitrant carbon (Lehmann et al. 2011). Carbon stabilization in the soil is involved in the global carbon cycle (Singh et al. 2018). However, not all the carbon inputs into soil resist to processes of mineralization, leaching, or erosion losses. Thus, soil carbon is assessed as labile (with a short half-life 1–20 years) or stable (20–100 years) (Goh 2004). Stable carbon stock is decisive to assess susceptibleness of soil organic carbon or services of ecosystems (Buytaert et al. 2011; Rolando et al. 2017; Yang et al. 2020). Biochar application is one of the ways to increase carbon sequestration and stabilization in soil, as it contains 20–80% of stable carbon which is not released into the atmosphere in the form of carbon dioxide within a couple of years (Llorach-Massana et al. 2017; Masek et al. 2011; McBeath et al. 2015). Compared to other organic matter resisting rapid mineralization and containing aromatic carbon compounds (such as lignin), biochar is primarily composed of fused aromatic carbon, hydrocarbons consisting of polycyclic aromatic compounds (Lehmann et al. 2011; Schmidt and Noack 2000). It has been reported that biochar application increases a humic-like fluorescent component in soil, and reduces co-localization of aromatic-C: polysaccharides-C. These changes, coupled with reduced C metabolism (decreased respiration), seem as important features of C stabilization in biochar-amended soils (Hernandez-Soriano et al. 2016). There are two forms of labile carbon, determined as dissolved organic carbon and fraction of unstable organic carbon (Al-Wabel et al. 2013). Biochar seems to be a material composed of micropores primarily consisting of aromatic carbon and less of carboxyl and phenolic carbon (Braida et al. 2003). The labile part of biochar can be indicated as volatile matter, and ash content which includes essential nutrients representing valuable sources for soil biota (Lehmann et al. 2011).

2.1 Effect of Feedstock on Biochar Properties

Biochar chemical composition is highly variable and depends mainly on its original feedstock and combustion settings (Spokas 2010).

A wide range of biochar is derived from all types of biological resources as well as from waste. Classification of biomass feedstocks to produce biochar can be based on different criteria such as initial moisture content, biomass growing conditions, or source of biomass (Fig. 1).

As a result, biochar may contain various amounts of elements, such as carbon, oxygen, hydrogen, nitrogen, sulfur, phosphorus, or heavy metals (Granatstein et al. 2009; Preston and Schmidt 2006). The general overview of elements loss from original biomass during the pyrolysis is shown in Fig. 2, in comparison with the initial biomass feedstock (Lehmann and Joseph 2015). In general, there is a vast difference between the contents of nutrients in biochar originating from the nutrient-rich feedstocks such as manure and sewage sludge from those prepared from lignin-based feedstocks (Yadav et al. 2018).

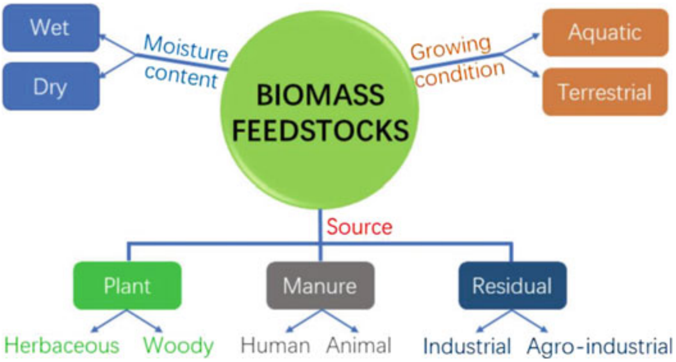


Fig. 1 Types of biomass feedstocks for biochar production. (Adopted from Yuan et al. 2019)

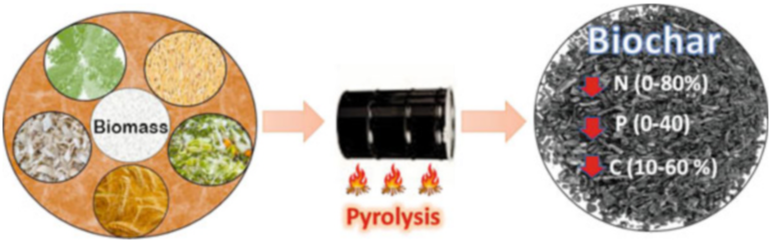


Fig. 2 Loss in nutrients from original biomass within the pyrolysis process. (Adopted from Lehmann and Joseph 2015)

Apart from elementary composition, the functional chemistry of biochar surfaces may differ depending on the original feedstock and pyrolysis conditions. The functional chemistry of biochar affects its sorption ability, and therefore it is important to understand how the production and ambient conditions affect functional groups in biochar. For example, it has been observed that high pyrolysis temperature reduces the number of functional groups, and consequently, biochar loses its negative charge, and its CEC decreases (Novak et al. 2009). On the other hand, the opposite situation occurs during the biochar weathering process, where enhancement of polar acid groups appears causing natural oxidation of its surface.

(Spokas 2013). According to a study by Li et al. (2013), carbonization cleaves hydroxyl and hydrogen groups at simultaneous aromatization which stabilizes biochar carbon making it less prone to mineralization.

Moreover, the feedstock also affects electrical conductivity and final pH (Singh et al. 2010), e.g. wheat straw feedstock was found to provide high CEC and low pH biochar, which is beneficial for soil organic matter (SOM) (Naeem et al. 2014). Wood feedstock biochar tends to have low to medium ash contents, while biochar derived from wheat or corn contains generally higher ash contents (Zhu et al. 2019). Higher content of minerals is negatively correlated with carbon in biochar (Gaskin

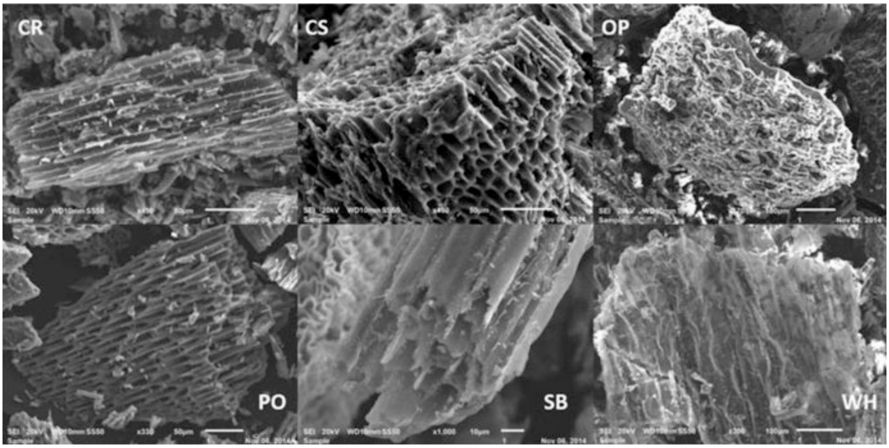


Fig. 3 SEM images of biochar samples (*CR* charcoal fines, *CS* coconut shell, *OP* orange peel, *PO* palm oil bunch, *SB* sugarcane bagasse, *WH* water hyacinth). (Adopted from Batista et al. 2018)

et al. 2008). The type of feedstock and pyrolysis temperature also significantly affects biochar yield in production. While low temperature results in a higher yield, higher temperature causes a lower yield, but the nature of the produced biochar is more recalcitrant (Jindo et al. 2014).

The appearance of BC is determined by the material used for its production. For illustrative purposes, scanning electron microscope (SEM) images of various BC samples derived from different feedstocks are shown in Fig. 3. Wood biochar retains its exoskeleton structure while manure–biochar is highly heterogeneous and comprises residues of digested food, seeds, and other fragments (Joseph et al. 2010). Thus, the feedstock is tightly related to biochar porosity, the character of pores, their size, surface area, and size layout (Downie et al. 2009).

2.2 Effect of Pyrolysis Temperature on Biochar Properties and Carbon

Chemical and physical properties of biochar depend on the feedstock type as well as on pyrolysis conditions (Nguyen et al. 2008; Jindo et al. 2014; Biederman and Harpole 2013; Novak et al. 2009). The suitable production procedure is decisive for biochar's further usability. By adjusting specific conditions of pyrolysis such as temperature, heating rate, and residence time, different biochar yields and composition can be obtained. Table 1 presents the influence of selected process conditions on biochar production and characterization (Bruckman et al. 2015). The relation between temperature and time during the pyrolysis process is depicted in Fig. 4.

The main factor affecting the properties of the final product is the temperature of pyrolysis, which does not usually exceed 700 °C (Lehmann and Joseph 2009). Pyrolysis carried out at low temperatures is beneficial for a higher yield of biochar,

Table 1 The effect of pyrolysis conditions on biochar production and characterization

Pyrolysis conditions	Specification	Effects
Temperature	Low (<400 °C)	More biochar, less C in biochar
	Moderate (~500 °C)	Less biochar, more C in biochar
	High (>700 °C)	Less biochar, more gas products
Heating rate	Low (<10 °C/min)	Slow heating, more biochar
	High (>300 °C/min)	Rapid heating, less biochar
Residence time	Low (<10 min)	Less carbonization, more C in biochar
	High (>1 h)	More carbonization, more C in biochar

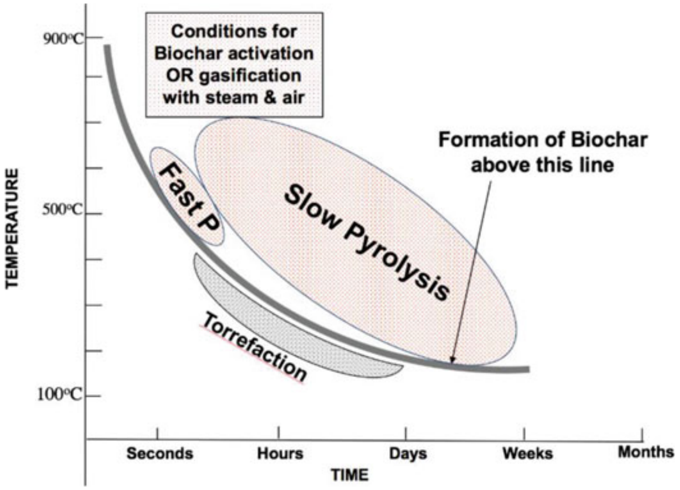


Fig. 4 Relation of time and temperature within the process of biochar production. (Adopted from Joseph et al. 2018)

better mineralization (Downie et al. 2009), and an increase in cation exchange capacity (CEC) (Mukherjee et al. 2011). Low-temperature production retains more nitrogen (Naeem et al. 2014) in biochar while high-temperature pyrolysis allows larger surface area (above 550 °C), higher carbon content, better sorption ability, and greater resistance to decomposition (Downie et al. 2009; Jindo et al. 2014; Naeem et al. 2014; Fischer and Glaser 2012). Higher temperature increases the pH (Mukherjee et al. 2011), decreases CEC, and raises concentrations of nutrients in biochar (Keiluweit et al. 2010). However, it also reduces the bioavailability of nutrients such as Ca, Mg, P, or K (Naeem et al. 2014). To reveal, how temperature affects physicochemical properties, the research by Jindo et al. (2014) assessed characteristics of a particular BC, e.g. apple branch-based biochar produced at 800°Cshowed surface area 12 m^2g^{-1}, yield 28%, pH 7. Biochar production proceeds at three stages: pre-pyrolysis, main-pyrolysis, and formation of carbonaceous soil products (Lee et al. 2010) (Fig. 5). The pyrolysis temperature is strongly correlated with changes in the structure and physicochemical properties of biochar.

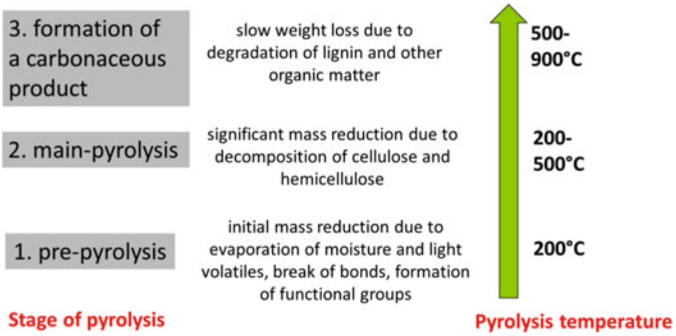


Fig. 5 Stages in biochar production

When using biochar in agriculture, the procedure could be adjusted in order to increase CEC and available nutrients and to improve soil fertility (Gaskin et al. 2008; Van Zwieten et al. 2010). It has been found that low-temperature biochar has the best results in agrochemical management (Gaskin et al. 2008). According to the study (Alotaibi and Schoenau 2019), low-temperature biochar (300 °C) exhibited better results in wheat growth and soil chemical properties (consistent positive influence on pH, CEC, and organic matter) while high-temperature biochar had a better effect on physical properties of soil (soil bulk density, total porosity, etc.). A lower temperature (up to 400 °C) is better either for stable aromatic backbone containing more C=O and C–H which can be used as nutrient exchanging sites (Novak et al. 2009; Glaser et al. 2002), or due to higher ash content of biochar contributing to better yield compared to recalcitrant biochar raising from higher temperature pyrolysis (Chan et al. 2008). The feedstock type and temperature also affect biochar properties in terms of the stable polycyclic aromatic carbon (SPAC) fraction content. The SPAC fraction controls resistance to mineralization and carbon stabilization. SPAC formation in biochar was $<20\%$ of the total organic carbon (TOC) at <450 °C and $> 80\%$ of TOC at above 600–700 °C (McBeath et al. 2015).

2.3 Cation/Anion Exchange Capacity, pH, and Carbon Mineralization

Cation exchange capacity (CEC) and anion exchange capacity (AEC) characterize the capacity of materials to exchange cations and anions, respectively. For biochar, CEC typically ranges between 77 and 119 cmol kg^{-1} (Lichtfouse 2014) while AEC varies between 0.602 and 27.7 cmol kg^{-1} (Lawrinenko and Laird 2015). These parameters are important for the extent of sorption abilities of biochar in soil that is influenced mainly by pH of the soil solution (Weil and Brady 2017). If the pH of the soil solution is above the point of zero biochar charge, biochar will be able to exchange cation nutrients because of the negative electrical charge on its surface (Mukherjee et al. 2011). Biochar immersed in water suspension is related to functional groups present on the surface of biochar. Functional groups are given by a carbonization procedure producing fused-ring and anomeric O-C-O or alkylated HCOH carbons depending on the indigenous feedstock (Li et al. 2013). CEC depends on the number of sites containing oxygen such as alcohol, carbonyl, and carboxyl groups bearing a negative charge and binding cations (Lawrinenko and Laird 2015). Nevertheless, not all acidic groups contribute to CEC. It has been found there were ten times fewer sites capable of binding cations than was the number of functional groups on the surface of biochar (Appel et al. 2003; Mukherjee et al. 2011). Coupled increases of CEC and decreases in carbon mineralization rates were observed under soil treatments with biochar, as the consequence of pH rising, and as an evidence of a relationship between carbon stabilization and high CEC (de Andrade et al. 2015).

Biochar pH measured in a water solution is alkaline to neutral (Solaiman and Anawar 2015). As other chemical properties, pH is highly dependent on biochar feedstock and production temperature. The high temperature usually provides biochar with higher pH while the lower temperature leads to reduced pH due to different ratio of dehydrogenation and aromatization in the process of pyrolysis (Li et al. 2013; Lichtfouse 2014; Mukherjee et al. 2011). Thus, high-temperature biochar can be used for liming, i.e. to increase the pH of acidic soils (Cheng et al. 2006, 2008; Chia et al. 2014; Liu et al. 2013; Granatstein et al. 2009). On the contrary, the addition of low-temperature biochar to already alkaline soils may eventually result in the decrease of soil pH (Lichtfouse 2014; Shenbagavalli and Mahimairaja 2012a; Gaskin et al. 2008; Liu and Zhang 2012). Soil solution pH can be affected by biochar. Low pH is not given only by a high concentration of H^+ but also by the presence of aluminium. Biochar has been found to not only adjust pH by its buffering capacity, but it can even sorb Al (Berek et al. 2011). However, the liming effect can be only short-term as the pH decreases during the weathering process (Spokas 2013). In addition, biochar in higher concentrations does not alter the soil pH as its exchangeable acidity is replaced by its buffering capacity (Solaiman and Anawar 2015). Thus, both the properties of biochar and its dosing should be taken into account when an increase of soil pH is one of the desired benefits of biochar application to soil.

Biochar pH may also affect short-term changes (negative or positive) in the mineralization rate of native SOC (Luo et al. 2011; Meena et al. 2020b). Higher pyrolysis temperature biochar shows decreased size of the priming effect, whereas lower temperature biochar is coupled with increased mineralization, which is further enhanced in the low pH soil and depressed in the high pH soil (Luo et al. 2011). The water-soluble components of biochar are the inducers of the priming effect for accelerated mineralization and decreased SOC, which is corroborated by observation of how water regimes (saturated, unsaturated and alternating conditions) that promote the differences in carbon mineralization and CEC in the BC materials (Nguyen and Lehmann 2009). Unsaturated and alternating conditions changed the CEC and O/C values of BCs and the evidenced increase in the oxidation rate was probably the key mechanism controlling biochar carbon stability (Nguyen and Lehmann 2009). With respect to the fact that biochar C mineralization is essentially a biological process, the pH is a fundamental determinator of microbial processes in soil. Whereas low-temperature BC increases the available and microbial biomass C concentration in both the low and high pH soil, high-temperature BC showed pronounced microbial colonization in the low pH soil but very low available C in the high pH soil (Luo et al. 2013). Other authors evidenced that the BC application to the soil can cause increases in soil pH due to labile carbon-derived changes in the soil microbial community (Farrell et al. 2013; Prayogo et al. 2014), for instance, increased abundance of Gram-negative bacteria (Prayogo et al. 2014) and actinobacteria (Prayogo et al. 2014; Liao et al. 2016). As it is known that most soil actinobacteria prefer and confer neutral to acidic soil pH (Basilio et al. 2003), these facts may link the higher microbial colonization of large surface high-temperature BC, which is coupled with low C mineralization rate, with higher pH soil.

2.4 Recalcitrance and Carbon Storage

Black carbon, which is similarly as biochar a purely natural origin matter, represents stable stock with a very slow rate of its turnover. It is because of its recalcitrance nature due to aromatic, graphitic, and refractory carbon (Glaser et al. 1998; Major et al. 2010a) in the form of aryl-C structures (Atkinson et al. 2010; Solomon et al. 2007). Black carbon is present in the sea in the form of sediments which are thousands of years older than the sediments without carbon (Masiello and Druffel 1998). Terrestrial land also has stabilized carbon storage as in the case of the aquatic environment (Glaser et al. 2001; Taketani et al. 2013).

Biochar is known to be a highly stable material, yet its initial decomposition has been observed by some researchers (Major et al. 2010a). For example, the study by Nguyen et al. (2008) observed that the decomposition of black carbon in soil originating from forest fire 2–100 years ago was rapid during the first 30 years, and then it slowed down. The most significant changes were observed on the surface of biochar with a decreasing tendency towards inner parts. Ageing caused gradual decomposition of biochar to CO_2, leaching, and dissolving of organic carbon. The nuclear magnetic resonance (NMR) analysis revealed higher aromaticity of SOM in charcoal-enriched soils. In contrast, the Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) results indicated an increased presence of lignin- and tannin-like compounds in the water-extractable SOM. It was evidenced that recent charcoal additions (>60 years) enhanced soil capacity to retain and stabilize C and N (Abdelrahman et al. 2018). Generally, biochar protects original soil organic matter and alleviates the priming effect (Granatstein et al. 2009). The protection of soil organic matter is caused mainly by refractory aryl-carbon structures (Atkinson et al. 2010; Solomon et al. 2007). Despite that our knowledge on the role of biochar in organic matter protection is incomplete, two main factors have been proposed to be relevant in this matter, i.e. the structure of small-size pores that mechanically prevent leaching and enzymatic breakdown of organic matter and the role of the chemical surface structure of biochar that depends on the character of either black carbon or biochar (Kasozi et al. 2010).

Table 2 Recalcitrance index (R_{50}) of different types of biochar (Harvey et al. 2012; Zhao et al. 2013)

Temperature of pyrolysis	Cellulose	Honey mesquite	Loblolly pine	Cordgrass	Pig manure	Wheat straw
unburnt	37	39	37	37	–	–
200 °**C**	37	38	37	39	46	41
400 °**C**	57	48	51	49	–	–
600 °**C**	61	53	56	52	71	71

The O/C ratio is considered as one of the essential factors of biochar recalcitrance (Harvey et al. 2012; Spokas 2010). Natural weathering leads to an increase in this ratio (Spokas 2013), and thus, biochar becomes more recalcitrant. A comprehensive study by Granatstein et al. (2009) reported biochar resistance time to be hundreds of years. Some types of biochar can be promptly mineralized, while others can remain intact thousands of years. It is difficult to determine biochar stability precisely as this would require long-term monitoring (Lehmann 2007). However, it appears that biochar with a low carbon content is more easily mineralized (Shenbagavalli and Mahimairaja 2012b). Similarly, biochar that contains aliphatic, apart from aromatic, structures of organic carbon are likely to be mineralized with higher speeds. The mineralization is processed from the outer parts; thus, another important aspect of biochar propensity to decomposition is the character of biochar particles (Lehmann 2007).

One of the methods developed to assess the propensity to degradation of biochar is the determination of recalcitrance index (R_{50}). The index relies on the thermal energy needed for the oxidation of biochar compared to graphite. There are three categories: R_{50} above 70, less than 70, and less than 50. The increasing number indicates higher recalcitrance; thus, a smaller portion of the carbon is mineralized within 1 year (Harvey et al. 2012). Examples of R_{50} values for different types of biochar are given in Table 2.

The carbon sequestration (CS) potential of the biochar is another tool to determine biochar recalcitrance. The CS is the amount of the original feedstock carbon that would be retained in biochar for long time periods upon addition to soil. This is calculated by subtracting the carbon lost during pyrolysis from the initial C in raw biomass and multiplying by the recalcitrance (R_{50}) of C in the biochar (Zhao et al. 2013).

To develop the biochar carbon stability, International Biochar Initiative (IBI) proposed a system of biochar classification based on carbon storage value in biochar (www.biochar-international.org). According to this system, the carbon storage value (sBC_{+100}) is referred to C_{org} in biochar and the estimated fraction of C_{org} in the biochar that remains stable in soil for more than 100 years (BC_{+100}). The BC_{+100} is based on the ratio of hydrogen to organic carbon (H/C_{org}) in biochar. The H/C_{org} ratio is an approximate measure of aromatic carbon structures in biochar. The sBC_{+100} can be used when estimating the long-term soil carbon sequestration potential of specific biochar. The sBC_{+100} is divided into 5 classes: 1st (<300 gkg), 2nd (300–400 gkg), 3rd (400–500 gkg), 4th (500–600 gkg), and 5th (>600 gkg). If long-term soil carbon sequestration is a goal, then biochar with a high sBC_{+100} would be desirable.

2.5 Role of Biochar Porosity in Improving Soil Functions and Soil Carbon Stabilization

One of the significant characteristics of biochar is its porosity, and related high surface area (Quilliam et al. 2013). Biochar pores are of different sizes and have different roles when biochar is applied to the soil. Larger pores promote airflow (Ezawa et al. 2002) and water retention capacity while the small ones surpass the transportation and adsorption abilities. The diameter of pores is dependent on the material used for biochar production. Charcoal fines have a pore size of 10 μm, oil palm bunch and sugarcane bagasse have a pore size of 6 μm, whereas activated biochar has a pore size up to few nanometres (Kasozi et al. 2010). Jindo et al. (2014) reported that the surface area from different feedstocks produced at different temperatures ranged between 5.6 and 545 m^2g^{-1}. The different feedstocks of biochar and their appearance are displayed in Fig. 3, e.g. water hyacinth biochar has coarse outer space as the pores are filled with ash (Batista et al. 2018); on the other hand, wood-based biochar is denser when compared to grass feedstock biochar (Brewer et al. 2014).

The porous structure of biochar determines its ability to sorb allelochemicals, such as phenols, which is evident from many studies (e.g. Jin et al. 2015). While larger pores are accessible for plants as a source of water or nutrients, tiny pores are sites for only chemical interactions where water cannot enter due to strong capillary forces (Antal and Grønli 2003; Brewer et al. 2014). The presence of charcoal particles elevated C and N stored in large particulate OM fractions (>20 mm), which presumably increased soil porosity and thus the soil capacity to retain water (Abdelrahman et al. 2018). Special issue in the topic of biochar porosity is the usage of biochar/charred materials as cost-effective and efficient adsorbents for CO_2 capture. Biochar is considered to be the most preferred carbon dioxide adsorbent material owing to its texture, modulative porosity and low cost, thus contributing also this way to the aspect of biochar-mediated carbon stabilization (Singh et al. 2019).

In addition, biochar is capable of providing a habitat for microorganisms, but the possibilities are limited (Jaafar et al. 2014). The most desirable place for fungal microorganisms to settle were tubular pores along biochar tissue remains, suggesting it as a route joining external and internal parts of biochar (Quilliam et al. 2013). Their experiment on woody feedstock biochar provided the evidence. The electron microscopy has shown extended fungal networks along the outer surface of biochar. Outer space of biochar was significantly more often colonized than inner pores.

3 Effect of Biochar Amendment on Soil Carbon Balance

The agriculture may profit from using biochar as a soil amendment, as it shows many positive impacts on soil. One of the essential notes on promising biochar effect is prevention from soil degradation by amending physical and chemical soil characteristics, which results not only in increased crop yield but also in sustainable soil management. Biochar application is considered to be useful agriculture management practise to support soil microbial community (Kolb et al. 2009) as it enriches the soil with available nutrients, such as carbon (Ippolito et al. 2016). Upon the long-term application, biochar interaction with soil enhances soil carbon storage via the sorption of SOM to biochar and physical protection (Zimmerman et al. 2011).

Biochar made under different conditions and from various feedstocks has various properties. Biochar with different properties can be utilized in solving a particular problem in the soil as the biochar properties can be designed according to the needs (Novak et al. 2009). Figure 6 shows the properties of individual types of biochar related to their pyrolysis temperature. The optimal temperature is between 500 and 600 °C, which is a range achieved by natural wildfire creating black carbon (Brady and Weil 2008).

3.1 Beneficial Effect of Biochar Application on Soil Carbon Storage

The addition of biochar changes the chemical and physical characteristics of the soil. These changes comprise alteration in the soil pH, increase in CEC and water retention capacity together with lower bulk density, promotion of the stability of organic matter and of crop yields (Jeffery et al. 2011; Liang et al. 2006; Nguyen et al.

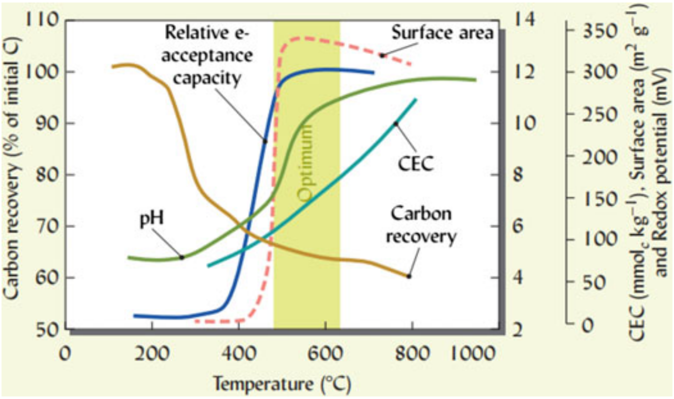


Fig. 6 Biochar properties depending on the temperature of pyrolysis. (Adopted from Brady and Weil 2008; Klüpfel et al. 2014; Lehmann 2007)

2018; Tryon 1948; Van Zwieten et al. 2010). One of the significant benefits of biochar application is that carbon is sequestered back to the soil, it also has fertilizing capabilities because it is a tool for retaining soil organic matter and nutrients (Gaskin et al. 2008). Biochar made of animal manure (so-called nutrient biochar) supports crop productivity and soil fertility. On the other hand, plant-based biochar (so-called structural biochar) improves the structure of soil but sometimes offsets chemical fertilizers (Sadaf et al. 2017). Biochar made of poultry litter seemed to have the best results for crop productivity while biochar based on lignin feedstock showed opposite results of decreased yield (Jeffery et al. 2011). Biochar can be used as an alternative to lime due to its ability to raise pH; however, higher expenditures must be expected (Granatstein et al. 2009). The opposite effect of different types of biochar was also reported for the carbon stabilization properties of biochar, where low temperature-pyrolysed biochar (250–400 °C) from grasses increased C mineralization rates in soils with lower organic C contents (in the early incubation stage – first 90 days). In contrast, soils combined with biochar produced at high temperatures (525–650 °C) showed lowered C mineralization during the later incubation stage (250–500 days) (Zimmerman et al. 2011).

3.1.1 Effect on Water Retention

Amendment of biochar could improve soil hydrological properties independence to biochar and soil conditions. Use of biochar could mean a viable option to improve moisture storage and water use efficiency for soils deficient in organic carbon in arid/semiarid zones (Omondi et al. 2016). An indirect effect of biochar on soil water retention and subsequent grain yield was caused even by promoting mycorrhiza during the period of drought (Solaiman et al. 2010). It seems that low-temperature pyrolysis provides biochar with better water retention because it creates biochar with more sites containing oxygen groups on its surface, determining hydrophobic properties (Alotaibi and Schoenau 2019). The water retention capacity highly depends on biochar feedstock. The study by Novak et al. (2009) assessed different feedstocks and found that switchgrass-made biochar showed the best results with regard to water retention capacity. However, the improvement of water retention depended not only on the character of biochar. Biochar can offset worse water retention only in soils with coarse structure. In fine-particles soil, the improvement was limited as clay particles clog pores (Wang et al. 2019).

Pores in biochar provide ample space retaining water due to capillary action. This can help to reduce soil propensity to drought. Water retention is also affected by the character of pores as biochar with a higher volume of pores can enhance water retention capacity, especially in soil with coarse structure. High doses of biochar led to the best results in improving soil structure such as a higher number of water-stable aggregates mean weight diameter and a lower coefficient of vulnerability (Juriga et al. 2018; Karhu et al. 2011).

Water retention is also affected by zeta potential and CEC. It is related to the content of hydrated ions adsorbed onto biochar. Biochar with a higher amount of substances with polar character shows better water holding capacity (Batista et al. 2018; Fischer and Glaser 2012; Ippolito et al. 2016; Liu et al. 2013). Water flow is improved as biochar application decreases soil bulk density (Abel et al. 2013) and positively affects saturated hydraulic conductivity and water infiltration (Major et al. 2010a), which may even support rooting (Lehmann et al. 2011). Such contributions to soil physical properties suggest that biochar is a suitable amendment to arid areas with a lack of water sources (Ippolito et al. 2016; Liu et al. 2017).

3.1.2 Effect on Soil Erosion

Biochar amendment significantly affects the physical properties of soil, which results in altered soil structure (Singh et al. 2018). The factor affecting the propensity of biochar to erosion is the ability to form macroaggregates, mean weight diameter of soil aggregates, bulk density, and stability of soil aggregates (Juriga et al. 2018). There is evidence that biochar can positively affect soil degradation by the impact on loosing soil particles. Its application significantly reduced the erosion of highly weathered soil while improving soil pH, cation exchange capacity, and microbial biomass carbon (Jien and Wang 2013). Its application decreased bulk density and enlarged soil aggregates, which is crucial for erosion resistance. Efficient improvement of soil was reported at a dose of 5% biochar (Jien and Wang 2013; Soinne et al. 2014). The results are supported by the study (Juriga et al. 2018), which found an increase in water-stable macro-aggregates after biochar amendment. Therefore, the optimal application dose of biochar to protect highly degraded soil in humid climate was set to 5% (Jien and Wang 2013). Biochar amendment to more weathered soils with high native SOM content may lead to more excellent stabilization of incorporated C and result in decreased loss of soil because of erosion and transport, as compared with the soils dominated by clays and low native SOM content (Kelly et al. 2017). However, there is a great risk of wind erosion of biochar particles within the simple surface application as biochar is composed of light particles that can be carried away by the wind. Such a situation can be expected in sandy soils (Verheijen et al. 2010).

3.2 Effect on Crop Yield and Economic Productivity in Agriculture

Agriculture productivity is often indicated as crop yield. It is difficult to predict if biochar addition will affect the productivity of crops as it largely depends on the type of biochar, climate, or soil conditions (Lehmann and Joseph 2009). The rate of yield increase is dependent on the dose of biochar. In the study estimating different agricultural systems (Liu et al. 2013), it was found that agricultural profit is achievable below 30 tha^{-1} of biochar dose with the mean profit between 10 and 11% (Jeffery et al. 2011; Liu et al. 2013). A comprehensive study analysing data on crop productivity (Jeffery et al. 2011) reports the average best dose of biochar to be 100 t ha^{-1}.

Biochar effect is more pronounced in acidic sandy soils than in alkaline clayey soils, which correlates with a higher yield of crops grown on dry land. It is related to the increased liming effect and improved water retention ability of the biochar-amended soils (Liu et al. 2013). Amendment of boreal clay soil with a high rate of biochar seems unviable from the farmer's perspective but could play a role in climate change mitigation, as it will likely serve as long-term C storage (Soinne et al. 2020).

Agriculture focused on non-food purposes often produces bioenergy. This leads to withdrawing of large amounts of biomass, resulting in the degradation and depletion of soils. Returning the organic matter in the form of biochar back to soils presents an effective solution for this issue where half of the carbon can be returned to the soil while improving the soil fertility (Lehmann 2007), which is the main factor of agriculture profitability. The meta-analysis (Biederman and Harpole 2013) investigated many studies assessing different biochar characteristics on the aboveground productivity of the crops. They found the biochar effect was more pronounced in tropical than in temperate zones. Manure- and grass-based biochar showed increased productivity. Many studies have confirmed that the lower temperature of pyrolysis had a more pronounced effect in agricultural use (Alotaibi and Schoenau 2019; Gaskin et al. 2008; Song and Guo 2012).

The study by Jindo et al. (2014) found that feedstock of biochar strongly correlated with crop yield. Wood-derived biochar provided worse results than biochar based on rice feedstock. A positive effect of biochar addition was observed in the case of the growth of rice (Nguyen et al. 2018). This positive effect can be attributed to the increased content of available nutrients (phosphorus and potassium) and CEC. Increased yield after biochar addition was also observed in the cultivation of maize (Major et al. 2010b; Yamato et al. 2006), wheat (Vaccari et al. 2011), soybean (Oka et al. 1993), carrots and beans (Rondon et al. 2004), and sorghum (Steiner et al. 2007). Nevertheless, it needs to be mentioned that most of the experiments using biochar amendments were carried out in the tropic climate. However, there is increasing evidence that the application of biochar can be beneficial for sustainable soil and productivity properties, also in a temperate climate (Cooper et al. 2020).

Studies by (Chan et al. 2007; Jeffery et al. 2011) provide a balanced picture of the impact of biochar use on agricultural yields. The worst results which were reported observed a 28% drop in yield (Jeffery et al. 2011). According to an in-depth evaluation (Brady and Weil 2008), it was estimated that a positive effect on yield reached a 30% increase and negative up to 20% decrease, but there were more results of positive effects with an average increase of 5–10%. Negative results can be explained by an increased content of volatile substances emerging during pyrolyses, such as pyrolytic substances from lignin or cellulose, gasses trapped inside biochar pores or low weight molecules including ketones, phenols, which can either stimulate or inhibit plant or microbial growth (Spokas et al. 2011). The study by Gale et al. (2016) suggests such labile substances negatively affect plants and soil microorganisms and are the reason for no or adverse effect of biochar addition. These unfavourable properties might be alleviated by weathering as the compounds are gradually lost from the soil and their toxicity reduced. Consequently, weathering may eventually lead to an increase in species diversity as some biota may be able to metabolize such substances, thus further mitigating their toxicity.

4 Biochar–Soil Community Interactions and Its Effect on Soil Carbon

4.1 Microorganisms

Biochar instantly interacts with roots, microorganisms, and soil organic matter in the soil. Microorganisms adapted to biochar presence were studied in the Amazonia. In the indigenous black earth, the most abundant phyla were *Actinobacteria, Acidobacteria, Verrucomicrobia,* and *Proteobacteria* (Taketani et al. 2013). However, the consequences and extent of the biochar effect on soil communities are not well understood (Downie et al. 2009; Joseph et al. 2010). For example, it is not clear under what circumstances biochar promote the growth of microorganisms in the soil (Gao et al. 2017; Chen et al. 2013; Ippolito et al. 2016; Lehmann et al. 2011). Yet, it becomes evident that soil enzyme activities, soil structure (Rillig and Mummey 2006), and nutrient cycling of mainly carbon and nitrogen are affected by the application of biochar to the soil (Chen et al. 2013; Steiner et al. 2008). Similarly, the amendment results in a direct impact on plants (Warnock et al. 2007), their growth (Graber et al. 2010; Kolton et al. 2011), or resistance to pathogens (Elad et al. 2010). Furthermore, biochar application may increase the activity of microorganisms and their biomass, crop yield, reduce nitrous oxide release, increase methane uptake by soil, and retain nutrients in the soil (Kolb et al. 2009; Naeem et al. 2014; Quilliam et al. 2013; Van Zwieten et al. 2009; Warnock et al. 2007).

Interestingly, experiments, where glucose was applied into soil amended with biochar, revealed increased microbial abundance but not respiration, which is similar to the microbial behaviour reported in Tera pretta (Steiner et al. 2004). This suggests that microorganisms are capable of reproduction at low-available soil organic matter environments with a sufficiency of nutrients (Fischer and Glaser 2012). Therefore, before the broad application of biochar, the land shall be inspected (Quilliam et al. 2013). It is mainly because the successful promotion of microorganisms depends on the properties of both biochar and soil. Soil analyses could comprise primarily physical and chemical characteristics, and attention should be paid to production methods and feedstock of biochar (Downie et al. 2009). Microbial changes, such as species composition and their activity, might be triggered even by the recalcitrant character of biochar as it largely depends on the number of available substances in the chromosphere. In the long term, the settlement of microorganisms can be enhanced by biochar addition along with gradual microbial and abiotic disintegration of biochar. The process can be accelerated by using powder biochar, which is decomposed and mineralized at a higher rate (Quilliam et al. 2013).

Biochar pores can provide shelter for bacteria. These may then be protected from predators (Ezawa et al. 2002). The pores must be large enough to be inhabited by bacteria or fungi but too small for predators to penetrate inside (Warnock et al. 2007). Not all the pores can be inhabitable by soil microbiota. In the study by Quilliam et al. (2013), the number of unprofitable pores reached 17%. However, these tiny pores provide a space for biochemical reactions. Microorganisms thrive well also in the vicinity of biochar even better when compared to its inner and outer surface (Quilliam et al. 2013).

From physical changes, reduced tensile strength is notable in biochar-amended soil (Chan et al. 2007), which enables better accessibility of nutrients for hyphae (Lehmann et al. 2011). Further, the increased surface area is probably the most significant factor in promoting mycorrhizal fungi (Ezawa et al. 2002) as it is an essential space for biological processes. Fragments of biochar act like soil aggregates as they protect organic matter and retain water and nutrients (Lehmann et al. 2011; Zimmerman et al. 2011). Though the significant effect of biochar on microorganisms is evident from many studies, the exact manner of the effect is still unknown. It is often caused by inconclusive results of field and laboratory experiments (Jones et al. 2011b; Quilliam et al. 2013; Ameloot et al. 2014).

Additionally, soil microorganisms may be affected by organic substances released from fresh biochar, either negatively or positively (Lehmann et al. 2011). Kolb et al. (2009) suggest that carbon is not a limiting factor in biochar amended soils; thus, microorganism biomass increase is dependent on other nutrients such as nitrogen and phosphorus.

Negative results could be related to short-term experiments investigating the application of fresh biochar. Sorption of cations and anions can affect the availability of carbon and other nutrients in fresh biochar. Thus, microorganisms are sometimes forced to use sources of C outside of biochar. Such a situation with a deficiency of nutrients potentially containing toxins can pose biochar as unhostile and poor nutrient habitat for microbes to live at (Quilliam et al. 2013) and/or cause problems related to low oxygen content and impaired conditions for aerobic microorganisms. Such issues might be solved by using powder biochar that seems to be more beneficial compared to large biochar clumps.

A comparison between microbiology of biochar incubated in medium without and with soil resulted in the evidence of greater fungal abundance in biochar incubated in a soil-less medium. Soil particles presented obstructions for fungal hyphae, and thus biochar colonization was more accessible in the absence of soil (Jaafar et al. 2014). Kolb et al. (2009) found different responses to biochar addition with regard to microbial biomass increase, depending on soil fertility, its texture, and nutrient availability. In contrast, other authors (Elzobair et al. 2016) found no impact on the microbial community, soil enzyme activity, or arbuscular mycorrhizal fungi colonization of roots. It has also been observed that biochar amendment can result in negative effects, especially in nutrient-poor sites. The experiment using biochar addition to reduce the number of phenolic compounds revealed that the positive effect was negated by reduced availability of nutrients sorbed on biochar. This resulted in the reduction of microbial biomass and inhibition of spruce seedlings (Glaser et al. 2002; Wallstedt et al. 2002). Another reason might be unfavourable living conditions for fungi, such as altered pH, heavy metals, or increased soil salinity (Killham and Firestone 1984). This illustrates that there is a number of factors that influence biochar–soil–microorganism interactions and add to the complexity of this issue. So far, our understanding of this issue is limited due to the mixed findings published so far and the general lack of knowledge on whether the amendment of biochar promotes or suppresses bacteria (Quilliam et al. 2013).

Ippolito et al. (2016) showed that upon the application of biochar, there was a slight decrease in Gram-positive bacteria and an increase in Gram-negative bacteria. Biochar addition also resulted in an increased rate of nitrification in sites low in nitrification ability, such as boreal forest. However, sites abundant in nitrification ability, such as grassland or agricultural soil, were not enhanced (DeLuca et al. 2015; Meena and Lal 2018; Rondon et al. 2007). This suggests that biochar affects even nitrification bacteria. Biochar seems to increase the rate of biological nitrogen fixation, which may help to reduce nitrogen inputs in agriculture. However, high rates (60 g per kg) of biochar resulted in adverse effects (Rondon et al. 2007), possibly caused by the lower availability of nitrogen in biochar-amended soil, which led to the stimulation of biological nitrogen fixation.

The first experiments carried out in the 1990s showed evidence that the addition of biochar to soil increased abundance in mycorrhizal fungi (Ishii and Kadoya 1994), followed by other studies confirming the same conclusion (e.g. Solaiman et al. 2010). Biochar interaction with mycorrhizal fungi may affect the physical and chemical properties of soils (Ishii and Kadoya 1994; Mori and Marjenah 2000; Solaiman et al. 2010). There is also a possibility of using biochar together with fungi, which could have a positive impact on soil quality (Warnock et al. 2007). Elzobair et al. (2016) studied soil community in arid soil and found that biochar did not negatively affect root colonization while the manure application did. The positive effect of biochar on mycorrhizal fungi is still not clear; it could result from the presence of a significant amount of carbon in biochar or might be induced by the properties and characteristics of the biochar itself (Warnock et al. 2007).

Biochar and mycorrhizal associations contribute to sustainable plant production, ecosystem restoration, and soil carbon sequestration by hyphae access of biochar microsites within biochar, that are too small for most plant roots to enter, and by subsequent translocation of nutrients to plants (Hammer et al. 2014). Thus, fungi can reach distant nutrients from their long hyphae far from roots (Saito and Marumoto 2002; Steiner et al. 2008). AMF can easily extend their extra-radical hyphae into charcoal buried in soil and sporulate in the porous particles (Saito and Marumoto 2002). Those pores may offer a microhabitat to the AMF, which can obtain nutrients through mycelia extended from roots (Nishio 1996). However, the ability to provide refuge for microorganisms does not occur several years after biochar application but requires a significantly longer time to occur (Quilliam et al. 2013).

The changes in the microbiological associations that were studied in a crop field after biochar application consisted of higher bacterial but lower fungal gene occurrence (Chen et al. 2013). It appears that fungi abundance does not increase following biochar addition if the environment contains sufficient amounts of nutrients (Lehmann et al. 2011) because, under such circumstances, the plants do not need to associate with mycorrhizal microorganisms.

4.2 Plants

Plant development and growth may be promoted by the addition of biochar via several mechanisms. Biochar speeds up the germination of seeds by its black colour changing thermo-dynamical characteristics of soil (Genesio et al. 2012) and by reducing in tensile strength of soil enabling easier penetration of first roots (Chan et al. 2007; Lehmann et al. 2011). It enhances water retention capacity and raises wilting point (the minimum amount of water in the soil that the plant requires not to wilt) (Abel et al. 2013; Laird et al. 2010), thus reducing moisture stress. Plant development is also affected by altered nutrition conditions, such as P and K (Biederman and Harpole 2013; Dempster et al. 2012; Nguyen et al. 2018).

Plant–soil–biochar interactions increase the stable C content in the soil. A study performed with ryegrass showed that field-aged biochar increased belowground recovery and stabilization of root-derived carbon. It also facilitated negative rhizosphere priming as a consequence of slowed soil organic carbon mineralization (SOC) in subtropical ferralsol (Weng et al. 2017). Graber et al. (2010) hypothesized that biochar stimulated plant growth in their study by alternation in the microbial community in soil, or by phytopathogenic compounds, which are toxic at high doses but stimulate plant growth at low concentrations. Kolton et al. (2011) found that biochar added to the community of microorganisms associated with plants had a positive effect on its growth and prosperity. Biochar was able to alleviate even unfavourable conditions of drought and salinity and thus supported plant growth, yield and increased photosynthesis (Ali et al. 2017).

There is also evidence that biochar may enhance plant protection against some pathogens, specifically some fungi (Elad et al. 2010; Meller Harel et al. 2012). Pathogen resistance is a consequence of cooperation between bacteria and roots known as induced systemic resistance. A possible way to explain the phenomena is the association between elicitors of microbial origin, which is promoted by added biochar (Kolton et al. 2011). Prendergast-Miller et al. (2013) revealed that roots are attracted to biochar via available nutrients such as nitrogen and phosphorus. Biochar acts either as a nutrient source for roots or influence nutrient availability and, thus, may affect roots in two different ways. It has been found that rhizosphere was more extent in soil amended with biochar indicating root's preference of soil comprising biochar (Prendergast-Miller et al. 2013).

4.3 Soil Fauna

Impact of soil fauna on the soil ecosystem is significant as it is a factor affecting the redistribution of nutrients from surface to subsoil (Domene 2016; Wilkinson et al. 2009). In general, biochar presence in soil is probably beneficial for soil fauna because it has been reported that mesofauna is more diverse and abundant in temperate zones naturally containing ancient charcoal (Uvarov 2000). Lower tensile strength caused by biochar addition (Chan et al. 2007) may enable more effortless mobility of vertebrate through soil (Lehmann et al. 2011). Biochar is ingested and released by soil organisms, though biochar is not considered to provide nutrients. As biochar goes through the digestive tract, it is enriched with microorganisms and enzymes. Those residues then resist on the surface of released biochar particles (Augustenborg et al. 2012; Domene 2016; Paz-Ferreiro et al. 2016).

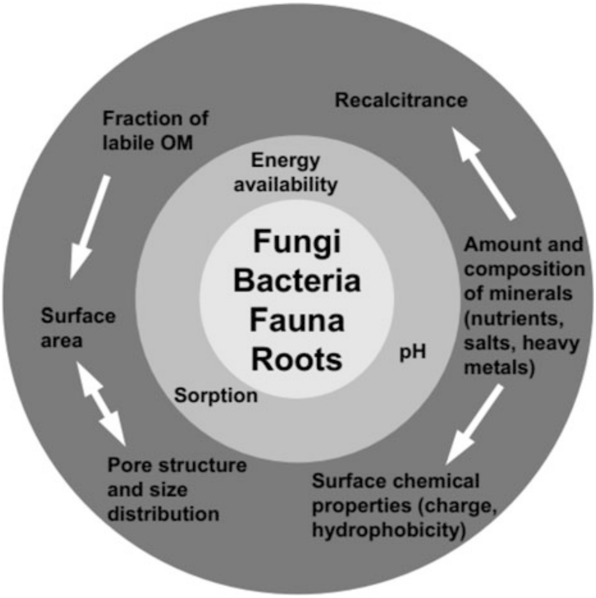
Several studies have focused on earthworms, which preferred soils amended with biochar (Van Zwieten et al. 2010), and on nematodes, which showed higher abundance in biochar-enriched soils (Matlack 2001). In addition, biochar was able to eliminate increased N_2O release by earthworms by 90% in soils rich in organic matter (Augustenborg et al. 2012). This effect can have a direct positive impact on agricultural profit as a co-application of biochar and earthworms increased productivity of crops in the study by Paz-Ferreiro et al. (2014).

Biochar bioactivation methodologies based on the mechanisms of coating biochar with enzymes represent an emerging and promising approach in biochar applications. The new earthworm-biochar model can be used as a framework to produce a new product "vermichar": vermicompost produced from the blended feedstock, earthworms, and biochar that may improve soil quality, enhance soil carbon storage, and remove soil contaminants (Sanchez-Hernandez et al. 2019).

5 Biochar Role in Metabolic Processes in Soil

The characteristics of biochar are interrelated and affect soil properties and soil biota. Thus, the addition of biochar may alter the nutrient cycling, soil physicochemical properties, species composition and their abundance, underground and above ground

Fig. 7 The overview of biochar effects on soil properties and soil biota. (Adopted from Lehmann et al. 2011)



biomass growth, and the overall health and quality of the soil ecosystem. Figure 7 displays these various attributes of biochar.

The addition of biochar to soil may provide additional benefits related to the increase in the content of stable organic matter. The addition of organic matter into soils rich in black carbon/biochar results in slower mineralization compared to black carbon-poor soils. Moreover, biochar-poor soils were also observed with higher mineralization rates of indigenous C (Liang et al. 2010).

Biochar presents a source of recalcitrant C that remains in soil over hundreds of years (Fischer and Glaser 2012). Thus, the application of biochar to soil contributes to C sequestration in soil and counteracts C emissions released by fossil fuels (Quilliam et al. 2013). The rate of organic mineralization is typically fast except the winter season, while biochar typically shows excellent stability, which is decisive in sustainable soil fertility (Yadav et al. 2018; Meena et al. 2020). Yet, the situation may be different on nutrient-poor sites where a particular fraction of nutrients in biochar is leachable. Under these specific conditions, the mineralization of organic matter can be supported by adding biochar (Wardle et al. 2008).

Furthermore, it has been found that mineralization rates of biochar can be accelerated by agriculture interventions such as sowing, planting, or ploughing with a direct effect on carbon storage (Lehmann et al. 2003b; Ameloot et al. 2014; Solaiman and Anawar 2015). It was observed that the application of biochar to forest soil increased the rate of nitrification due to the presence of phenolic compounds in biochar. In the case of agricultural soils, the addition of biochar inhibited or promoted C mineralization rates (Berglund et al. 2004; Dempster et al. 2012; Jones et al. 2011b; Wardle et al. 2008; Dodor et al. 2018; Zimmerman et al. 2011). Jones et al. (2011b) suggest that the alterations in soil physical properties induced by biochar addition have no significant effect on the rate of soil respiration.

Soil enzymes react variably to the presence of biochar in soil. The results of studies are often inconsistent and unclear with regard to the relationships between biochar and soil enzymes (Bailey et al. 2011). However, it is evident that biochar can alter enzyme activities (Foster et al. 2016; Chen et al. 2013). For example, a decrease in the activities of β-glucosidase and an increase in the activity of alkaline phosphatase and dehydrogenase were observed in biochar-amended soils. Changes in enzymatic activities were further observed by (Foster et al. 2016), where the activities of α-1,4-glucosidase, β-D-cellobiohydrolase, and β-1,4-N-acetylglucosaminidase increased while the activities of β-1,4-glucosidase and phosphatase significantly decreased upon biochar addition to soil. These results point to the shift in behalf of bacteria (Chen et al. 2013), which can be related to increased enzyme activities. On the other hand, decreased enzyme activities can occur especially in the case of biochar with high porosity and specific surface due to the blocking or sorption of enzymes substrates (Bailey et al. 2011; Lammirato et al. 2011).

5.1 Nutrients and Their Availability

Biochar cannot be considered as a primary supply of nutrients. It enriches the soil with several beneficial elements and minerals; thus, its main prospective is to condition soil properties (Glaser et al. 2002; Lehmann et al. 2003a; Shenbagavalli and Mahimairaja 2012b). Nevertheless, biochar amendment results in increased concentration of soil elements, such as P, K, N_{total}, and C (Biederman and Harpole 2013; Nguyen et al. 2018). Content of nutrients is highly dependent upon feedstock (Shenbagavalli and Mahimairaja 2012b). The nutrient and chemical values of biochar made of different feedstock are presented in Table 3. The resulting properties of biochar such as pH and CEC further influence the availability of nutrients in soils to which the biochar was added (Yadav et al. 2018). For example, biochar addition to soil usually results in higher pH, which in turn increases Ca and Mg intake by plants and crop yield (Major et al. 2010a). However, there are reports of widely variable effects of biochar on soil organic carbon and C sequestration among different agricultural soils despite the same biochar dose was used. Following this observation, it was concluded that site-specific soil properties must be carefully considered to maximize long-term soil organic carbon sequestration after biochar application (Bi et al. 2020).

The availability of nitrogen with regard to biochar use in the soil is discussible. While some authors reported low availability of N (bound into the heterocycles) (Gaskin et al. 2008), the others found that N was available for plants especially in

Table 3 Chemical characteristics of biochar prepared from different feedstocks (Shenbagavalli and Mahimairaja 2012b)

Factor	Paddy straw	Maize stover	Coconut shell	Groundnut shell	Coir waste	Prosopis wood
pH (1:5 solid water suspension)	9.68	9.42	9.18	9.30	9.40	7.57
EC (dSm^{-1}) (1: 5 soil water extract)	2.41	4.18	0.73	0.39	3.25	1.3
CEC (cmol kg^{-1})	8.2	6.5	12.5	5.4	3.2	16
Exchangeable acidity (mmol kg^{-1})	22	27	32	14	9.5	49
Total organic carbon (g kg^{-1})	540	830	910	770	760	940
Total nitrogen (g kg^{-1})	10.5	9.2	9.4	11	8.5	1.12
C/N ratio	51.4	90.2	96.8	70	89.4	83.9
Total phosphorus (g kg^{-1})	1.2	2.9	3.2	0.6	1.5	1.06
Total potassium (g kg^{-1})	2.4	6.7	10.4	6.2	5.3	29
Sodium (g kg^{-1})	14	21.5	16.8	5.2	9.6	38
Calcium (g kg^{-1})	4.5	5.6	8.5	3.2	1.8	11
Magnesium (g kg^{-1})	6.2	4.3	5.8	2.1	1.4	0.36

manure–feedstock biochar (Clough et al. 2013; Chan et al. 2008), where the available nitrogen content is related to hydrolysable forms, e.g. amino acids (Wang et al. 2012). Cantrell et al. (2012) assessed different manure-based biochar and found that the most substantial amounts of volatile matter, carbon, and energy were in dairy manure-based biochar while poultry manure-based biochar contained the highest amounts of S, P, and N contents.

Charred material contains a large amount of aromatic C resistant to microbial mineralization. With higher temperatures of pyrolysis, lower mineralization rates of biochar can be expected (Baldock and Smernik 2002). This can potentially result in adverse effects on plant growth, especially in the case of biochar with a high C/N ratio, where N availability can be reduced. The resulting mineralization or immobilization of N is driven by N content in the original soil and by the C/N ratio of the amended soil. The C/N ratio of <20 leads to N mineralization, while higher ratios lead to the immobilization of N (Dodor et al. 2018). Thus, if the biochar amendment high in C/N ratio is applied to soil depleted from nitrogen, immobilization of mineral nitrogen immobilization can be expected.

The higher dose of biochar caused a greater concentration of extractable phosphorus at the simultaneous decrease in extractable nitrogen (Kolb et al. 2009). However, the nitrogen was increased during incubation time, which can be related to the increase in microbial biomass and subsequent mineralization. This finding was verified by other findings by Biederman and Harpole (2013) who analysed an exhaustive number of studies and concluded that soil is enhanced by P and K following the addition of biochar.

The nutrients are released as the charred material is weathered. Nevertheless, Dempster et al. (2012) found out that the addition of either fresh or aged biochar is unlikely to affect the mineralization of small N substances. However, there is an alteration difference in fresh and weathered biochar. It seems that fresh biochar is more abundant in elements and minerals compared to weathered biochar that had lower contents of Ca, Mg, C, and P and increased O/C ratios (Spokas 2013). These factors significantly impact production yields (Warnock et al. 2007) as also observed by Gao et al. (2017) who found a decrease in dissolved organic C and available N contents despite the increase of their total contents. They suggest that nutrients were adsorbed to biochar surface where P bioavailability could be controlled by biochar-induced surface organic matter stabilization or adsorption/desorption of P associated with organo-mineral complexes (Gao and DeLuca 2018). Figure 8 shows the various effects of biochar on nutrients turnover.

5.2 Sorption Ability of Biochar and Carbon Binding

Soil profits from biochar application via biochar ability to sorb/immobilize nutrients and contaminants. Thus, biochar application to soil indirectly impacts the quality of water and of agricultural watersheds (Laird et al. 2009).

The electrical surface charge of biochar causes high cation exchange capacity resulting in strong binding ability of cations (Mg^{2+}, Ca^{2+}, K^+, and NH_4^+) available

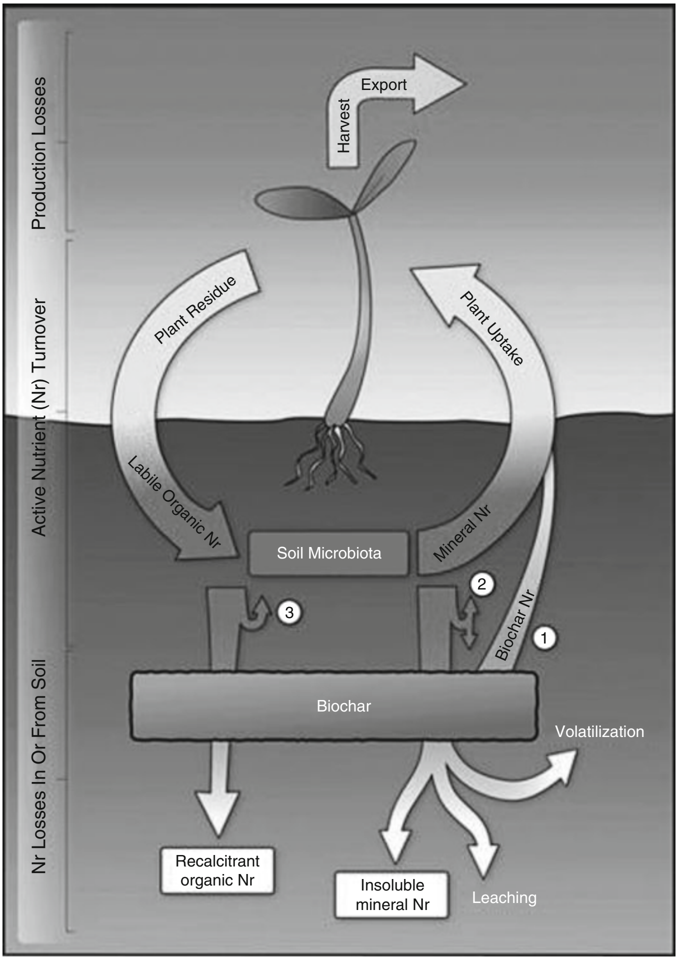


Fig. 8 Effect of biochar on nutrients (Nr) turnover (Adopted from DeLuca et al. 2015)

for plants (Gai et al. 2014; Manyà 2012; Meena et al. 2020a; Yuan et al. 2011) or anion exchange capacity which is less known and is adhesive mainly for negatively charged phosphates (Lawrinenko and Laird 2015; Mukherjee et al. 2011).

Biochar produced from different feedstocks and temperatures of pyrolysis characterizes with different surface area and pore volume, which are important physical properties affecting the sorption capacity of given biochar. Higher surface area and porosity enhance sorption capacity of biochar. In Table 4, there are some examples of surface area and pore volume for different biochar.

Biochar addition starts immediate interaction with organic substances (Jones et al. 2011a; Quilliam et al. 2013; Smernik 2009) through chemical bonds such as hydrogen, cation-anion and covalent bonds (Joseph et al. 2010). Nutrients, e.g. P or N in the form of nitrates are also absorbed to biochar which helps to slow down

Table 4 Surface area and pore volume for different biochar

Type of feedstock	Pyrolysis temperature (°C)	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	References
Broiler litter	350	60	0.000	Uchimiya et al. (2010)
	700	94	0.018	
Orange peel	350	51	0.010	Chen and Chen (2009)
	700	201	0.035	
Soybean Stover	300	5.6	–	Ahmad et al. (2012)
	700	420.3	0.190	
Pine needles	400	112.4	0.044	Chen et al. (2008)
	700	236.4	0.095	
Rapeseed plant	400	16	1.244	Karaosmanoğlu et al. (2000)
	700	19.3	1.254	
Sewage sludge	300	4.5	0.010	Ahmad et al. (2012)
	700	54.8	0.050	

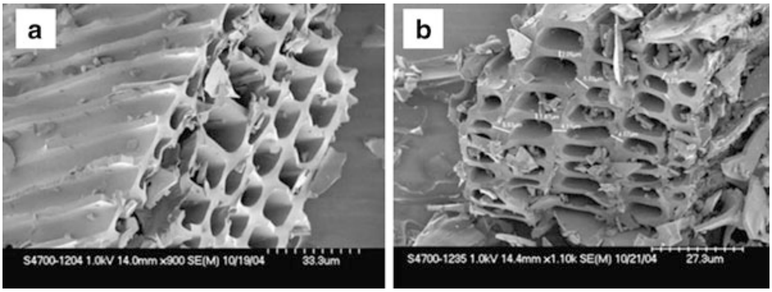


Fig. 9 Biochar with high (**a**) and low (**b**) sorption capacity. (Adopted from DeLuca et al. 2015)

their leaching (Laird et al. 2010; Prendergast-Miller et al. 2013; Granatstein et al. 2009). This is consistent with this study (Gao et al. 2017) which reported an increased content of nutrients, such as total carbon and nitrogen, but a decreased amount of dissolved organic carbon and available nitrogen. The sorption properties of biochar are illustrated in Fig. 9, showing an example of fresh/aged biochar with high/low sorption capacity. The letter “a” refers to fresh immature biochar where pores are still unclogged with particles and are ready to bind substances and particles. The letter “b” indicates pores of old biochar occluded with particles of organic matter bound to its surface (DeLuca et al. 2015). Keech et al. (2005) claimed in his study that sorption highly depends on the number of macropores rather than on their density.

Sorption ability is given mainly by the surface of the biochar. Fresh biochar is hydrophobic with not many polar sites. Processes of oxidation and exposure to water create groups containing oxygen, mainly carboxyl. Biochar surface is abundant in carbon, and therefore, it tends to be hydrophobic and allows sorption of non-polar substances depending on layout and concertation of functional sites (Lawrinenko and Laird 2015). However, its surface is both hydrophobic and hydrophilic, characterized by acidity and basicity (Lehmann and Joseph 2009; Zhu et al. 2018). The study on sorption activity of catechol, a highly hydrophilic contaminant, and humic acid, a less hydrophilic part of organic matter, assessed whether biochar could protect organic matter and be used in soil remediation. It was observed that biochar produced under high temperature showed better sorption activity to catechol into micropores with specific sorption-sites. Humic acid was less sorbed due to its exclusion from micropores (Kasozi et al. 2010).

The sorption ability of biochar is relevant not only form the viewpoint of nutrients but also with regard to a plethora of other (in)organic substances such as pesticides (Yu et al. 2009; Zheng et al. 2010), polycyclic aromatic hydrocarbons (Chen and Yuan 2011), and herbicides (Granatstein et al. 2009). Promising results were also observed regarding the (partial) immobilization of highly mobile and toxic elements such as cadmium and arsenic (Beesley and Marmiroli 2011). Additionally, the immobilization of heavy metals resulted in increased yield and plant biomass in biochar amended soil (Park et al. 2011). Sorption capability of biochar may mitigate pollution of water bodies by preventing leaching of N and P from soil to water. Another indirect effect of nutrient retention is the reduced need for fertilizers (Lehmann 2007; Troy et al. 2014). The addition of biochar to soil resulted in the elimination of stress associated with higher salt concentrations in soil. Excessive concentrations of salts tied to biochar which implies that biochar can be used as a tool for alleviating salt stress in agriculture (Ali et al. 2017; Amini et al. 2015; Solaiman and Anawar 2015).

5.3 Biochar Potential to Affect Soil Carbon Stock

Soil organic carbon is introduced to the soil by organisms enduring therefore a short time to millennia. SOC is a major part of soil organic matter providing nutrients and retaining water availability, fertility, and crop productivity (Lefèvre et al. 2017). Carbon is lost as dissolved organic carbon by leaching or is transformed to CO_2 or CH_4 and released back to the atmosphere (Lefèvre et al. 2017). Global warming is tightly joined with the carbon cycle. Biochar could affect the global carbon cycle by removing excessive carbon originated from the burning of fossil fuels from the atmosphere (Nguyen et al. 2008). Change of natural systems into agriculturally used land leads to a rapid increase in CO_2 emissions and depletes soil from organic carbon, especially by deforestation. This seems to be a critical factor in the global carbon cycle (Zhang et al. 2018). Intensive agriculture, arable land and changes in land use exhale greenhouse gases (GHGs). However, the soil management is able to even increase the stock of carbon, e.g. in the form of thermally stabilized sequestered carbon present in biochar (Ippolito et al. 2016; Sohi et al. 2010). Precious organic matter is lost due to burning or disposing of large amounts of residues, which could have been transformed to biochar (Yadav et al. 2018).

As already mentioned, biochar is anthropogenically obtained by pyrolysis. The process can effectively solve two issues. It offers renewable energy and alternative solution to bio-waste disposal. The thermo-chemical procedure converts waste into valuable product omitting CO_2 emissions (Granatstein et al. 2009). Carbon added in the form of biochar into soil resists there much longer than if initial feedstock material is mixed with soil, thus increases the content of recalcitrant carbonaceous substances (Yadav et al. 2018) and of soil carbon stock in soils (Granatstein et al. 2009). However, crucial for carbon sequestration are the consequences and potential effects of biochar on soil communities that are yet not completely understood (Downie et al. 2009; Joseph et al. 2010). The amount of carbon sequestered in soil depends on C content in biochar. Biochar made from plant-based materials is higher in carbon stock; biochar based on herbaceous or fibrous feedstocks comprises of approx. 65% of C and have a high content of N, and wood-based biochar contains approx. 75% of C with the C/N ratio ranging between 178 and 588. According to Gaskin et al. (2008), poultry-litter biochar contains 40% of C while pine-biochar contains 78% of C. In the study by Foster et al. (2016), biochar dose of 30 t ha^{-1} increased the total carbon in soil by 80%.

Inconsistent results have been reported with regard to the priming effects of biochar that were shown to be positive (Dodor et al. 2018; Jones et al. 2011b; Luo et al. 2011) as well negative (Ippolito et al. 2016; Jones et al. 2011b; Zimmerman et al. 2011). Carbon mineralization was shown to be primarily influenced by the temperature of pyrolysis at which biochar is produced; a higher temperature can be expected to result in negative priming effects after longer incubation times, e.g. 200 days (Fischer and Glaser 2012). The duration of the experiment seems to play a significant role. Short-term experiments can result in higher priming effects compared to long-term studies when the labile organic matter of biochar is depleted. In the experiment by Cross and Sohi (2011), the priming effect increased within 2 weeks of the experiment compared to non-amended soil. The positive priming effect decreased with increasing pyrolysis temperature. It has been found that the initial increase in priming effect is caused by the labile part of organic matter present in biochar and not by the organic matter present in the soil. Thus, carbon addition does not trigger higher mineralization of organic matter in the soil. This also may explain the inconsistencies between studies resulting in either increased or decreased priming effects or mineralization after biochar addition. Short-term CO_2 increase is a consequence of mineralization of an equal amount of organic C originating in the added biochar (Jones et al. 2011b; Luo et al. 2011). Mineralization of C can be enhanced by limited access to nutrients (Cross and Sohi 2011). However, a long-term observation implied a decrease in soil organic matter mineralization and reduced CO_2 release (Jones et al. 2011b; Zimmerman et al. 2011). In another study, the decreased values of SOC mineralization (carbon sequestration) were explained by the accelerated conversion of SOC into dissolved inorganic C and by the sorption of labile organic C (LOC) and microorganisms onto biochar (Luo et al. 2016).

All carbon types in biochar are not stable. There is also mobile carbon, especially in young biochar, coming from oil produced during pyrolysis. Smith et al. (2010)

found out that only about 10% of extractable carbon is mineralized to CO_2 as the substances precipice to larger molecules, they probably become a part of recalcitrant carbon stock in the soil. The initial short-termed increase in CO_2 release may result from microbial mineralization of unstable carbon which could be contained in immature biochar (Jones et al. 2011b; Smith et al. 2010; Zimmerman 2010). Cross and Sohi (2011) investigated whether biochar addition initializes mineralization of C already present in the soil. The results confirmed that all the evolved CO_2 originated from the labile fraction in the added biochar.

The global C cycle is related to black carbon as it slows down its turnover by carbon sequestration (Major et al. 2010a). Woolf et al. (2010) estimated that the biochar could eliminate 12% of CO_2 originating from anthropogenic sources. On average, one metric ton of biochar added to the soil can offset 2.93 metric tons of CO_2 (Granatstein et al. 2009). The study by Laird (2008) assumes that the USA can produce an enormous amount of biomass. Implementation of such biomass into biochar could save 25% fuel oil enabling permanent sequestration and save 10% of CO_2 emissions. The study about smokeless biomass pyrolysis consider the creation of biochar carbon energy storage reserves: it was estimated that about 428 Gt of carbon could be worldwide annually stored as a biochar carbon into agricultural soils (1411 million hectares) (Lee et al. 2010).

Carbon dioxide is captivated by photosynthesis in the form of organic biomass which is then used to create biochar (Renner 2007). The biochar created by pyrolysis blocks the fast decomposition of biomass feedstock. The outcome of the high-temperature process serves as energy bypassing GHGs emissions and provides a soil amendment to return carbon (Woolf et al. 2010). The complex process of carbon cycling is shown in Fig. 10. Types of biochar produced at conditions of zero-oxygen are less studied. Their energy and carbon turnover demand more investigation for agronomic compensation (Sohi et al. 2010). The zero-oxygen pyrolysis is advantageous even for better sorption of volatile compounds released during biochar production (Spokas et al. 2011). However, Woolf et al. (2010) suggested not to clear forests or rainforest to get feedstock for biochar production because the carbon pay-back would take many years, and this land-use would be highly ineffective. They suggested abandoned and degraded land to be prospective for energy and biochar production intentions.

One of the non-carbon GHGs is a nitrous oxide that is even more potent GHG than CO_2, and its main release can be attributed to the use of nitrogen fertilizers (Renner 2007). It has been found that fluxes of N_2O and CH_4 may be reduced due to biochar application to soil (Van Zwieten et al. 2010; Augustenborg et al. 2012; Rondon et al. 2006). The mechanisms behind this action are not clear, but most probably, a mix of various biotic and abiotic factors come into play here, along with other factors such as climate, soil type, land use and properties of the biochar applied (Van Zwieten et al. 2009). The ability to retain N_2O is likely affected by the type of biochar. While biochar made from poultry litter or high-temperature grass feedstock showed no emissions of N_2O, low-temperature waste grass biochar releases 100% emissions compared to control (Rondon et al. 2006).

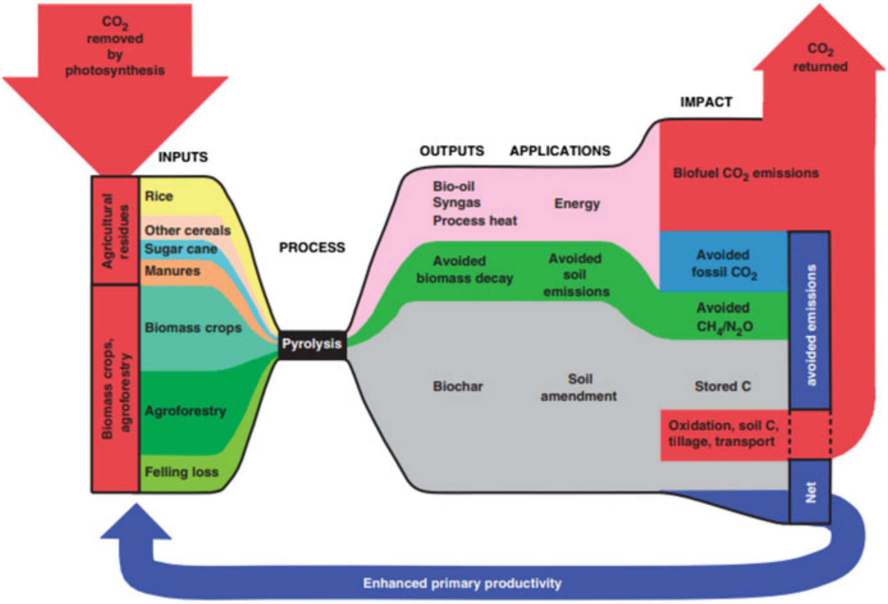


Fig. 10 Sustainable carbon cycling using biochar. (Adopted from Woolf et al. 2010)

6 Interaction of Biochar with Other Amendments and Impact on Soil Carbon

The beneficial properties of biochar can be enhanced by the synergic effect using co-application of biochar together with other soil amendments. Biochar may increase the efficiency of mineral fertilizers by promoting nutrient retention and eliminating their environmental threats. Thus, it may address many problems of nowadays agriculture and environment (Naeem et al. 2014). It may even contribute to economic savings because of the reduced amount of fertilizers applied to land (Lehmann 2007; Troy et al. 2014). Despite the fact that the biochar can increase nutrients in the soil, it is still deficient in nutrients, and possible effectivity of its combination with other soil amendments is obvious. Accumulation and retention of nitrogen in the rhizosphere were improved by the combined effect of biochar and mineral fertilizer (KNO_3, $(NH_4)_2SO_4$, and urea) resulting in higher microbial abundance and pH in soil (Yu et al. 2018). Used co-application of NPK and biochar have increased the nutrients and yield of wheat. It resulted in higher N content, microbial carbon, and microbial nitrogen which are the main driving factors having a positive impact on soil microbial community and activity of soil enzymes (Song et al. 2018). Experiments with combined application of biochar and mineral fertilizers confirmed that this is a promising strategy for increased yield without unnecessary loss in nitrogen by leaching. Biochar combined with nitrogen caused alteration in soil organic matter and soil structure that affected in soil improvement. The co-application increased the content of organic carbon. On the other hand, a particular combination of biochar and nitrogen caused a drop in humic and fulvic acids (Juriga et al. 2018). It also significantly increased yield as the biochar promoted mineral nitrogen fertilizer efficiency (Chan et al. 2007). The enhancing effect of combined biochar and mineral fertilizer application may lie in the ability of biochar to retain some nitrous compounds (Granatstein et al. 2009), to prevent nitrogen leaching and to protect nutrients in the soil. It has been found that biochar addition improved N uptake and biomass production. The experiment was carried out using wheat in fertilized ferrosol (Van Zwieten et al. 2010). On the other hand, biochar did not show any improvement without added fertilizers (Van Zwieten et al. 2010). Solaiman et al. (2010) applied biochar to soil together with mycorrhizal fungi and mineral fertilizer. The yield was significantly increased in sandy soil. There was even noted improved resistance to drought.

Application of pig manure caused an increase in the leaching of nutrients, such as nitrates and organic carbon. The amendment of manure-fertilized soil by wood-feedstock biochar reduced the leaching as biochar retained nutrients (Troy et al. 2014). Brtnicky et al. (2019) observed the decrease of soil microbial carbon and dehydrogenase activity 3 years after the incorporation of biochar (from agricultural waste) into the soil. On the other hand, the highest values were reached after the co-application of biochar with cattle manure in their study. Dodor et al. (2018) have studied the effect of the simultaneous application of biochar and cattle manure on carbon mineralization in sandy soil. Pure biochar and manure application caused an increase in positive priming effect by 45–125%. However, their combined amendment has decreased C decomposition caused due to labile C adsorption and net N immobilization. The priming effect was negative by 35%. A completely different situation was observed by Ippolito et al. (2016). They found a positive priming effect by the co-application of manure with biochar and negative priming effect increasing with the application of biochar only. These contradictory findings could have arisen from the different nature of the biochar used (hardwood biochar with a very high C/N ratio versus rice-husk biochar). Elzobair et al. (2016) observed short-term effects when the manure–biochar mixture was applied to arid soils. While the application of biochar alone did not affect microorganism, the sole application of manure caused an increase in some microbial characteristics and a decrease in AMF colonization.

Nevertheless, some studies show no improvement upon the co-application of manure and biochar. For instance, in the study by Nguyen et al. (2018) cow manure was co-applied with biochar, which resulted in an initial decrease of nitrates and their subsequent increase after the manure was mineralized (Ippolito et al. 2016). The co-application of compost-biochar mixtures is another type of relevant mixed amendments. The components in the mixed amendments interact with each other and have similar effects on soil properties. These synergetic interactions enhance the efficiency of the improvement of soil properties (Wu et al. 2017). Liu and Zhang (2012) reported that the synergism provides positive impacts on soil organic matter, nutrients, and water retention capacity. In the study by Wei et al. (2014), the combination arising from composting the tomato stalk and chicken manure was

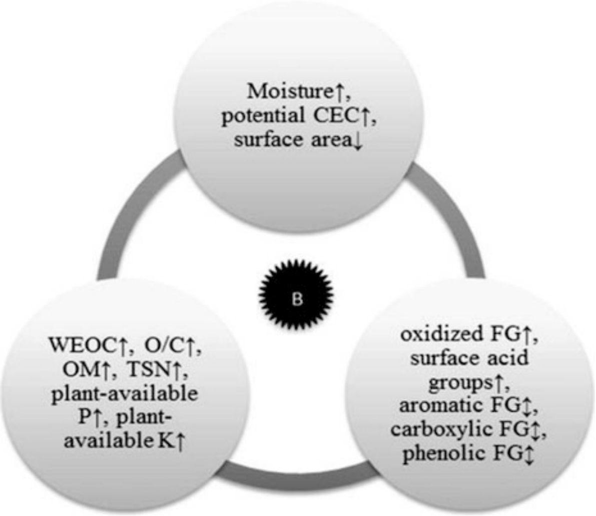


Fig. 11 The effects of biochar on composting. (Adopted from Wu et al. 2017)
CEC Cation exchange capacity, *WOEC* water-extractable organic carbon, *O/C* oxygen/carbon ratio, *OM* organic matter, *TSN* total soluble nitrogen, *FG* functional group, ↑ increase, ↓ decrease, ⍰ sometimes increase and sometimes decrease

reported to be most effective. Changes in the microbial diversity and an increase in the C/N ratio together with volatile fatty acids were observed (Wei et al. 2014). Doan et al. (2015) found a positive effect of co-amendment of biochar with vermicompost, which resulted in higher N retention and protection from erosion and nitrogen leaching. In addition to the benefits above, the co-application of compost and biochar was shown to reduce the bioavailability of toxins (Zeng et al. 2015). Wu et al. (2017) summarized the main positive effects arising from of co-application of biochar and compost which were: changes in physicochemical soil properties, reduction of greenhouse emissions, promotion of plant growth, and alteration of microbial activities (Fig. 11).

Because humic substances are important for carbon sequestration in soil, Jindo et al. (2016) have found that the addition of biochar to composted manure improved the formation and the composition of humic substances. Biochar addition reinforced the stability of the fractions of humic substances in compost. The fulvic acids were enriched in carboxylic and aromatic groups, while humic acids characterized by more condensed molecular structure. This could increase the stability of humic substances when compost blended with biochar is applied as soil organic amendment. Wang et al. (2014) have observed more intensive humification in pig manure compost amended with biochar. With the ^{13}C-NMR spectroscopy higher O-alkyl C/alkyl C ratio and higher aromaticity for humic acids have been revealed.

7 Future Perspective

The future perspective can be seen in designing enriched biochar to improve soil physical and chemical as well as biological properties. The procedure imitating weathering process coats biochar with other substances which could have a significant positive effect on the soil ecosystem. Co-application of available fertilizers (mineral or organic) with biochar or enriched biochar can be persuaded as a solution to offset biochar and fertilizer deficiencies. The fertilizer supplies accessible nutrients available to plants and biochar can sequester depleted elements and prevent leaching of the added ones. This leads to increased crop yields and, simultaneously, alleviation of water pollution by excessive amounts of nutrients.

8 Conclusion

The literature suggests that biochar presents a promising solution for the high energy demands and carbon sequestration efforts, in addition to its positive effects on the functions of the soil ecosystem (Biederman and Harpole 2013). Unlike to organic residues that are mineralized in usually less than 30 years (Liu et al. 2013; Lehmann et al. 2006), biochar withstands microbial decomposition and weathering processes and thus contributes to the soil carbon stock in a long-term perspective, prevent soil degradation, and supports the idea of sustainable agriculture.

However, when the results of individual studies are compared, contradictory findings can be found. This can be explained by the plethora of properties of biochar arising from the initial feedstock and production conditions as well as from the highly diverse and complex systems of soils that are further affected by climate, moisture conditions, and soil biota. Nevertheless, biochar application to soil is associated with many benefits that are likely to outweigh the potential risks, especially if our understanding of biochar effects in soils further improves. In this respect, the co-application of biochar with fertilizers and the use of enriched biochar offers promising ways for increasing the positive effects of biochar for soils and carbon stabilization.

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Glomalin: A Key Indicator for Soil Carbon Stabilization

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Abstract

In the last decades, many studies were addressed focusing on soil protection that helps sequestration and stabilization of organic carbon in soil aggregates. Soil aggregates are an association of primary soil particles, bacteria, fungi, plant root

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and soil organic matter. Plant root provides a carbon source for arbuscular mycorrhizal fungi (AMF) present in soil aggregates. AMF produces a glycoprotein glomalin which is hydrophobic, insoluble, and recalcitrant in nature. Glomalin plays a vital role in the stabilization of soil aggregates. Greater stability of soil aggregates leads to a larger amount of protected organic carbon in the soil. Thus, glomalin-related soil protein can be considered as a potential contributor in the stabilization of soil organic carbon. In the present chapter, the different aspects of glomalin composition, production, role in soil, recalcitrant nature, potential role in soil carbon locking up and stabilization are summarized and discussed.

Keywords

Glomalin · Arbuscular mycorrhizal fungi (AMF) · Carbon · Heavy metal · Biotic stress

Abbreviations

AMF	Arbuscular Mycorrhizal Fungi
BRSP	Bradford Reactive Soil Protein
GRSP	Glomalin-Related Soil Protein
HSP60	Heat Shock Protein 60
OM	Organic Matter
SOC	Soil Organic Carbon
SOM	Soil Organic Matter

1 Introduction

In the last 20 years, soil protection research has been focused on frequently discussed issues such as soil erosion, structural deterioration, potentially toxic elements, loss of biological diversity and depletion of SOM. These adverse factors directly lead to soil degradation and reduced fertility and impaired non-production function. The amount of organic matter or some of its fractions is an essential indicator of soil quality and health. Several positive effects of glomalin on soil have been demonstrated since its discovery in late 1990. In particular, they include the improvement of soil aggregation and structure stabilization, increased wind and water erosion resistance (Wuest et al. 2005), improved water regime, suppressing toxicity of pollutants (Vodnik et al. 2008), sequestration and stabilization of carbon (Nie et al. 2007), resistance to stress conditions (Hammer and Rillig 2011; Latef et al. 2016) and subsequent promotion of plant growth (Adesemoye et al. 2008). SOM affects AMF diversity and richness. Glomalin protein plays a crucial role in the stabilization of soil aggregates and their effect on SOC stabilization (Wilson et al. 2009).

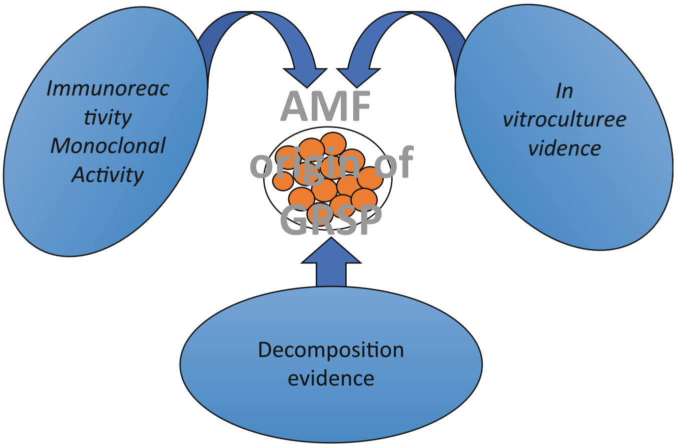


Fig. 1 Evidence suggesting the production of glomalin-related soil proteins by arbuscular mycorrhizal fungi. (Adopted from Singh et al. 2012)

Glomalin has been discovered and described by Sara Wright in 1996 during her research on vesicular-AMF. The substance was determined as a glycoprotein produced especially by arbuscular mycorrhizal-hyphae and to a limited extent also by spores. It was relatively late discovered, due to its specific properties: hydrophobicity, thermostability, and recalcitrance (Johnson and Gehring 2007; Sousa et al. 2012b). In the experimental study, glomalin was detected only in samples where roots were colonized with AMF (Smith and Read 2008b).

Figure 1 displays lines of evidence leading to the AMF origin of GRSP. Firstly, glomalin detection is proposed by methods using a monoclonal antibody which is specific to fungi (Thornton and Gilligan 1999). Secondly, decomposition tests prove that when AMF is eliminated, significant glomalin decline can be detected (Steinberg and Rillig 2003). Thirdly, the monoclonal body is used for the detection of easily extractable and immunoreactive GRSP. It reacts only with AMF members eliminating cross-reaction with other fungal species. MAb32B11 monoclonal antibody also provides the detection of spores and hyphae (Wright et al. 1996).

GRSP concentration in the soil varies depending on sites, which was linked mainly to pH variations (Wang et al. 2014). It has also been found that glomalin is primarily stored in the topsoil, and its content is lower in deeper soil layers (Wang et al. 2017). No glomalin was determined deeper than 140 cm. Further, it was detected even in rivers (Franzluebbers et al. 2000; Harner et al. 2004; Rillig et al. 2001a; Staddon 2005; Wang et al. 2018). Sites more abundant with AMF host plants or containing more carbon available for fungi are frequently detected with higher glomalin content (Treseder and Turner 2007). Seasonal variation in glomalin concentration is negligible (Steinberg and Rillig 2003). A typical concentration is 2–15 mg.g^{-1} of soil. However, it is determined by the soil age and moisture content.

Table 1 GRSP content in different environments (modified) (Vlček and Pohanka 2020)

Environment	GRSP ($mg.g^{-1}$)	References
Agricultural land	0.3–0.7	Wright and Anderson (2000) and Wuest et al. (2005)
Boreal forest	1.1	Treseder et al. (2004)
Desert	0.003–0.13	Rillig et al. (2003a) and Treseder and Turner (2007)
Temperate forest	0.60–5.8	Nichols and Wright (2005), Steinberg and Rillig (2003) and Treseder and Turner (2007)
Temperate grassland	0.23–2.5	Batten et al. (2005), Lutgen et al. (2003) and Nichols and Wright (2005)
Tropical rainforest	2.6–13.5	Lovelock et al. (2004) and Treseder and Turner (2007)
Antarctic region	0.007–0.15	Pohanka and Vlcek (2018)

There are cases of higher concentrations measured, e.g. Hawaiian soil samples (more than 100 mg. g^{-1} of soil) while lower glomalin concentration was found in soils of arid regions, less than 1 $mg.g^{-1}$ of soil (Bird et al. 2002; Rillig et al. 2001b; Wright et al. 1998). The presence of glomalin at different sites was summarized by (Vlček and Pohanka 2020) (Table 1).

Quality and quantity of SOM strongly correlate with glomalin (Šarapatka et al. 2019). Therefore, glomalin indicates changes in soil, its degradation or erosion. Glomalin is proposed to be a suitable index of soil fertility, especially in arid soil. It was found that BRSP content positively correlates with the incidence of SOC, soil enzymes, nitrogen and phosphorus (Bai et al. 2009). Moreover, the same authors found that BRSP was a little higher in arable compared to the desert land. Despite lower BRSP content in a desert, the ratio of BRSP to SOC was much higher there, suggesting it could be an indicative level of fertility, especially in a desert. The ratio of glomalin to the total organic matter could be even used also as an indicator of soil degradation (Sharifi et al. 2018; Meena et al. 2020). Glomalin contributes to organic carbon stock and is significantly correlated to nitrogen in all soil types (Wilson et al. 2009). Land-use changes have a significant impact on the content of glomalin in soil. It was found that its content is much lower in agriculturally used land compared to native or afforested land (Rillig et al. 2003b). Thus, the authors suggest that it offers a possibility of glomalin content to become a useful sensitive indicator of land-use changes.

The present chapter targets its interest to a fraction of the SOM – a protein referred to as glomalin and summarized and discussed different aspects of glomalin and its composition, production, role in soil, recalcitrant nature, potential role in soil carbon sequestration and stabilization.

2 Determination and Terminology of Glomalin

The term “glomalin” can be used only to a protein encoded by the putative gene of AMF (Rillig 2004b). The chemical structure of glomalin remains still elusive and is only operationally and vaguely defined as a product of extraction procedure. Therefore, the term “glomalin-related soil protein” is used because the isolation of specific protein glomalin has not been carried out yet. The glomalin association with other soil proteins is well characterized by (Zbiral et al. 2017). Extraction is always burdened with non-glomalin impurities; thus, GRSP has been proposed to define the correlation of glomalin content (Rillig 2004a).

Humic acids and GRSP have similar extraction procedure; therefore, these substances are co-extracted (Schindler et al. 2007). There is a study (Gillespie et al. 2011) employing sensitive methods to characterize the chemical bonds (X-ray absorption near edge structure spectroscopy, pyrolysis-field ionization mass spectrometry). The proteomic study helps to differentiate GRSP mixture that contains humic acids, proteins of non-mycorrhizal origin and abundant heat-stable proteins related to soil and bacteria (Gillespie et al. 2011). Important substances from the view of availability, concentration or determination of glomalin are secondary metabolites, mainly tannins (Halvorson and Gonzalez 2006; Vlček and Pohanka 2020). In all the methods applied, the product is still a mixture of glomalin with co-extracted molecules, but their mutual link has not been defined yet (Schindler et al. 2007).

GRSP was first operationally determined by a monoclonal and glomalin-specific monoclonal antibody (MAb32B11) bound to a protein present in disrupted spores of *Glomus intraradices* (Wright and Upadhyaya 1996). The substances detected by the immunological method are called “immunoreactive soil protein”. The outline of Glomalin Formal terminology is in Table 2 (Rillig 2004a).

Generally, all methods for total GRSP and soil proteins estimation suffer from impurities. Thus, methods are considered only as semi-quantitative (Redmile-Gordon et al. 2013). The most frequently used is the citrate method (Wright and Upadhyaya 1996) carried out under harsh conditions, including autoclaving of soil in a sodium citrate buffer at 121 °C, and followed by glomalin precipitation using trichloroacetic acid. The obtained extracts may be purified using 100 mM sodium borate solution (Schindler et al. 2007). Consequently, Bradford assay is used for its quantitative analysis (Nichols 2003; Treseder and Turner 2007). The improvement is sometimes applied to distinguish the proteinaceous materials from co-extracted humic materials using the modified Lowry microplate method (Redmile-Gordon et al. 2013). The particular substances related to glomalin are stated in Table 2.

Moreover, the GRSP can be classified as easily extractable and residual fractions (Lovelock et al. 2004). The easily extractable part is obtained at mild extraction conditions (121 °C, 30 min, 20 mM citrate, pH 7) in an autoclave, while the residual fractions at harsher extraction conditions (121 °C, 50 mM citrate, pH 8) in 1-h increments until the supernatant is colourless. The extracts are precipitated using hydrochloric acid (Schindler et al. 2007). This is beneficial mainly if the amount of C and N is measured because trichloracetic acid may bind to proteinaceous substances,

Table 2 Formal terminology for glomalin (Rillig 2004a)

Current usage	Identity	Proposal name/ usage	Justification
Total glomalin	BRSP (after autoclave/ citrate extraction)	BRSP	Bradford assay is non-specific for particular protein
Easily extractable glomalin	BRSP (easily extracted; autoclave/citrate)	EE-BSRP (easily extracted; BRSP)	Bradford assay is non-specific for particular protein
Immunoreactive glomalin	Immunoreactive (MAb32B11) soil protein (after autoclave/citrate extraction)	Immunoreactive (MAb32B11) soil protein	There is the possibility of cross-protein reactivity in soil
Immunoreactive easily extractable glomalin	Immunoreactive (MAb32B11) soil protein (easily extracted; autoclave/ citrate)	Easily extracted immunoreactive (MAb32B11) soil protein	There is the possibility of cross-protein reactivity in soil
Glomalin	Immunoreactive (MAb32B11) soil protein (easily extracted; autoclave/ citrate extraction)	GRSP	"Glomalin" in the currently used sense refers to very different entities

and thus it gives inaccurate C contents (Wright and Upadhyaya 1996). Easily extractable GRSP is believed to be produced newly or to be a recently decomposed fraction of GRSP while the total GRSP is considered to be an aged and more stable fraction of GRSP (Wright and Upadhyaya 1996).

The near-infrared spectroscopy detection method can be applied to replace the laborious high-pressure extraction of GRSP (Zbiral et al. 2017). The results showed fast GRSP determination during the simultaneous determination of other parameters such as oxidizable carbon, total carbon and nitrogen. Near-infrared spectroscopy GRSP determination method has also been successfully used in work by Heinze et al. (2013).

3 Composition

Glomalin is a protein that is very difficult to be extracted. It is often indicated as BRSP or GRSP containing some other additional proteins (Nichols 2003; Rillig et al. 2001b; Treseder and Turner 2007) and phenolic substances, such as tannins. The impurities represent up to 40% of plant litter and maybe a part of many biochemical processes in the soil (Appel 1993; Fierer et al. 2001; Hättenschwiler and Vitousek 2000; Kraus et al. 2003). Glomalin extracted from the soil contains 28–45% C, 0.9–7.3% N, and 0.03–0.1% P (Sousa et al. 2012b; Wang et al. 2017). Glomalin may also encompass metal ions depending on soil type (Huang et al. 2011; Gadkar and Rillig 2006). It may cover nearly a third of the soil carbon level and 1–9% of bound iron (Nichols and Wright 2005) which is responsible for the red colour of glomalin extract (Wright et al. 1998). Elemental analysis results combined with infrared and nuclear magnetic resonance spectroscopy data of GRSP revealed a high content of aromatic (42–49%) and carboxyl groups (24–30%), carbohydrate (4–16%) and low aliphatic substances (4–11%), which is not typical for glycoproteins but is closer to the molecular feature of humic acids (Schindler et al. 2007).

Glomalin was discovered to possess three N-glycosylation sites in its structure (Gadkar and Rillig 2006). Its structure seems to be a complex of N-oligosaccharides (Wright et al. 1998). There are even aliphatic amino acids with methyl, methylene and methines groups, polymeric with metal ions with methine being part of the peptide backbone (N–CH–C=O) (Rillig et al. 2001b). Metal ions are joined to auto-fluorescent compounds. It was reported that GRSP comprised of 49 fluorescent substances, seven functional groups, and some other elements (Wang et al. 2015b). The same study emphasizes that the composition and characterization of GRSP are more complicated than it was thought formerly. However, its biochemical structure has not been fully revealed yet (Gao et al. 2019).

Another knowledge gap on glomalin structure is whether it is a substance of consistent composition. There is a theory suggesting that glomalin composition is variable with quite substantial differences depending on sites of glomalin occurrence (Wang et al. 2014). The hypothesis is encouraged by the study assessing GRSP content difference on farmland and 30-years afforested farmland (Wang et al. 2015a). It highlights that the soil properties were significantly affected not only by the difference in GRSP concentration but also by its variable composition. There is another interesting hypothesis of Magdoff and Weil (2004) based on different organic carbon concentration in glomalin (27.9–43.1%). They stated glomalin could not be a product of an expressed gene but rather a mixture of organic matter with parts reactive to immune probes.

4 Glomalin Pathways

GRSP production is under the control of hyphae (Rillig and Steinberg 2002; Singh et al. 2012). Gadkar and Rillig (2006) reported that cell walls of hyphae contain the most considerable amount of glomalin and spores rather than secreted out of cell walls (Driver et al. 2005; Wright and Upadhyaya 1996). Results indicate that a primary function of glomalin is in fungal hyphae, and its other impact to the soil is secondary (Purin and Rillig 2007). It has been confirmed by a study examining different physical condition on hyphae growth. The glomalin primary function in hyphae comprises tolerance to grazing stress (Hammer and Rillig 2011), enhanced soil aggregate stability as hyphae grow better in aggregated soil (Rillig and Steinberg 2002) or toxicity protection (Ferrol et al. 2009; Lenoir et al. 2016). Based on this system, the presence of glomalin has been confirmed together with the putative gene for glomalin in proliferating mycelia (Gadkar and Rillig 2006; Purin and Rillig 2007). Even though glomalin is an AMF metabolite produced by hyphae, its concentration is not correlated to their length (Lutgen et al. 2003; Treseder and Turner 2007).

Glomalin is a homologue of HSP60, which was suggested based on a high identity of the amino acid sequence (Gadkar and Rillig 2006). HSP60 is a product of prokaryotic or eukaryotic cells in conditions of environmental stress (Chen et al. 2015). The glomalin encoding gene was indicated as GiHsp 60 and was isolated *in vitro* from *Glomus intraradices* (Gadkar and Rillig 2006). Thus, the discovered homology suggested that the original function of glomalin might be the protection of fungi (Lenoir et al. 2016).

The way how the glomalin is stored in the soil is unknown. There are two possible pathways. The first one assumes glomalin is a permanent part of the AMF and is released into the soil after hyphae disintegration. In such a case, it is an essential functional component of AMF (fungal tissue) with negligible impact on soil (Driver et al. 2005). The second less possible route is the secretion of glomalin as a metabolite by AMF hyphae. The latter would indicate certain mobility of glomalin within the soil. However, it could have been more readily decomposed by the soil microflora (St-Arnaud et al. 1996). Nevertheless, it was measured that 80% of glomalin is located in hyphae (Driver et al. 2005). However, a complex structure of soil suggests there might be some other factors or linkages entering the glomalin-soil relationship (Rillig 2004a).

5 Arbuscular Mycorrhizal Fungi

Soil microorganisms associated with plant roots are referred to as AMF. They are creating symbiotic relation, which is beneficial for both fungi and plants. This association of a plant and microorganism represents the most widespread type of symbiosis (Smith and Read 2008b). AMF group belongs to the phylum *Glomeromycota* (Schussler et al. 2001), which is also the most significant group of fungi producing high amounts of glomalin, compared to other groups (Wright and Upadhyaya 1996). Phylogenetic analysis revealed common ancestors for Ascomycota and Basidiomycota with AMF. Some fossils records of *Glomeromycota arbuscula* suggest that AMF played an essential role in forming terrestrial ecosystems already 250–400 million years ago (Harper et al. 2013; Redecker 2000; Remy et al. 1994; Schussler et al. 2001). These records suggest that *Glomeromycota* were participating in the colonization of terrestrial ecosystems by plants in its earliest stages, which supports the theory that they assist in the process (Blackwell 2000; Pirozynski and Malloch 1975; Simon et al. 1993).

Taxonomy of *Glomeromycota* is relatively young. Before 1974, the majority of AMF was classified in the genus *Endogone*. Since then (Trappe and Gerdemann 1979), AMF has been classified into four different genera: *Glomus*, *Sclerocystis*, *Acaulospora*, and *Gigaspora*. The recent taxonomy classification in detail was published by (Young 2012). Taxonomical classification of *Glomeromycota* is visualized in Fig. 2.

Phylum *Glomeromycota* currently includes about 220 described species (Blaszkowski et al. 2012). Lee et al. (2013) reported that there are more than 240 species, and their genetic and functional diversity is much richer than the

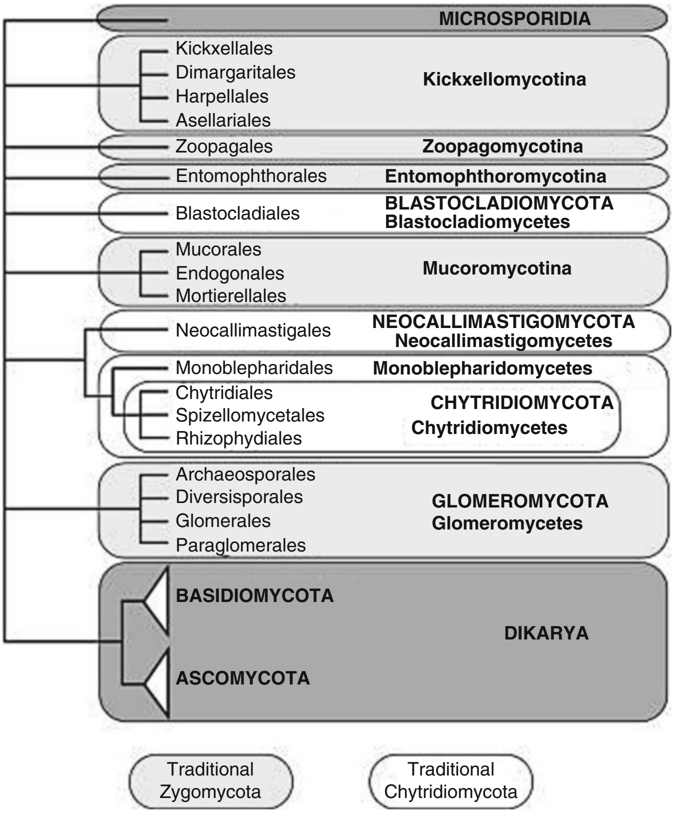


Fig. 2 Taxonomy of fungi. Branch lengths are not proportional to genetic distances. (Adopted from Hibbett et al. 2007)

morphological diversity. Most of them were defined by the morphology of the spore, which has turned it out to be a wrong way of classification (Morton and Redecker 2001; Redecker 2000). Morphology of spores is insufficient to assess the diversity of fungi as their genome is highly diverse. There are differences even within a species as they can vary in the effect on a symbiotic plant. Functional diversity might be probably resulting from a combination of plant and AMF (Lee et al. 2013). Recently, DNA sequencing was used to reduce the number of taxa.

Arbuscular mycorrhiza can be found in 70–90% (Blaszkowski et al. 2012) or 80% (Fitter et al. 2000; Smith and Read 2008a) of vascular plants (i.e. most of *Embryophyte* species). AMF has adapted symbionts of more than 200,000 plant species (Lee et al. 2013). AMF has a very low host specificity (Smith and Read 2008b). The mixtures of AMF very often colonized a single plant (Helgason et al. 1999), but the combinations of plant-fungus symbionts are known to be more or less favourable.

Crops which are highly dependent on AMF are, for example, corn (*Zea mays* L.) and flax (*Linum usitatissimum* L.). Mycorrhiza is advantageous for wheat (*Triticum* spp.), barley (*Hordeum* spp.), oats (*Avena sativa* L.), legumes (*Leguminosae*) or potato (*Solanum tuberosum* L.) but they do not show dependency on it. There are also few plants, which do not form a symbiosis with the AMF at all: among them are families *Brassicaceae*, *Amaranthaceae, Polygonaceae,* and the better-known crops mustard (*Brassica juncea* L.), rape (*Brassica napus* L.), sugar beet (*Beta vulgaris* L.), spinach (*Spinacia oleracea* L.), and buckwheat (*Fagopyrum esculentum* Moench) (Harley and Smith 1983; Plenchette et al. 1983; Thingstrup et al. 1999).

Generally, *Leguminosae* plants are capable of binding air nitrogen. Thus they can saturate their own N need and even supplement soil with N (Mikanová and Šimon 2013). This is crucial for agricultural productivity as non-*Leguminosae* are supplemented with nitrogen via *Leguminosae* (Stern 1993), especially when growing mixed culture, i.e. *Leguminosae* and non-*Leguminosae* at the same land. The transfer of nitrogen from nitrogen binding plants is indicated as rhizodeposition (Fustec et al. 2010). It has been found out that transfer between the plant species provided by mycorrhizal bridges joining roots of plants grown in mixed culture (Bethlenfalvay et al. 1991; Laberge et al. 2010; Meng et al. 2015; Walder et al. 2012; Meena et al. 2018).

Arbuscular mycorrhiza is essential for the proper functions of the majority of terrestrial ecosystems, e.g. boreal forests or heath (Read 1991). Differential advantage in succession within the ecosystem is provided by AMF (van der Heijden et al. 1998). Arbuscular mycorrhiza is endomycorrhiza, i.e. the root cells of vascular plants are penetrated with the fungus (see Fig. 3). Inside the root cells, a pouch (vesicle)-shaped storage organs are built. Moreover, a tree-like structure (arbusculus) is formed beyond the root when the fungus invades the roots (Fig. 4). The highly specialized symbiosis or mutualism was formerly known as “vesicle-arbuscular mycorrhiza”. The mutualistic relationship enables AMF to enrich plants with minerals and elements from the soil (mainly phosphorus), and the plant provides organic substances from the photosynthesis.

As can be seen in Fig. 3, upon ectomycorrhizae (green) plant root cells are not penetrated by the fungal hyphae, but a covering mantle of fungal tissue around the root is created. In contrast, endomycorrhizal fungi (yellow) penetrate cortical cells and create arbuscules and vesicles. At ectoendomycorrhiza, both the covering mantle and cell penetration may occur.

The root surface is due to the hyphae increased by up to 80% (Millner and Wright 2002). Hence, it gives the plant an access to distant nutrients and elements that are hardly mobile in the soil. Nutrients are also more bio-available, e.g. phosphorus. AMF assists in litter decay and transports already released nutrients to the plant (Nuccio et al. 2013). The ways how nutrients can be easily reached are shortening distances, increasing solubility and affinity of P ions and increasing the area of its absorption (Bolan 1991). In addition to a direct positive effect on plant growth, arbuscular mycorrhiza benefits the plant habitat indirectly by improving the soil properties, in particular the ability to enhance the stability of soil aggregates (Bayer et al. 2001). AMF itself presents 5–50% of microbial soil biomass and significantly

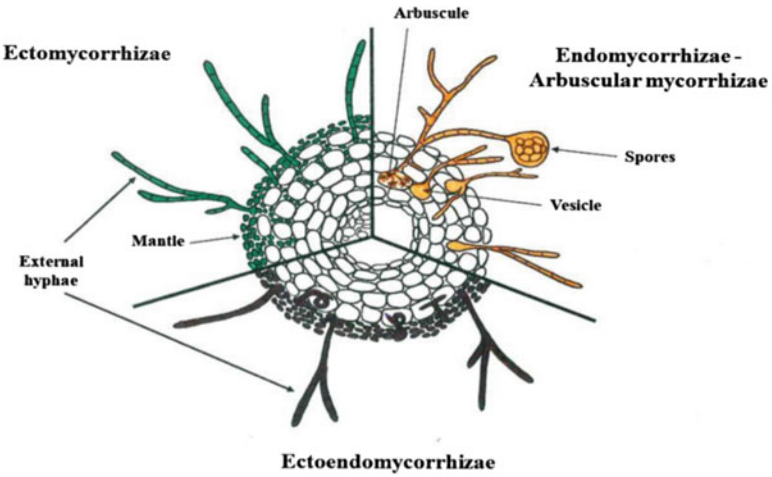


Fig. 3 Three different types of symbiotic associations between a mycorrhizal fungus and plant roots. (Adopted from Ganugi et al. 2019)

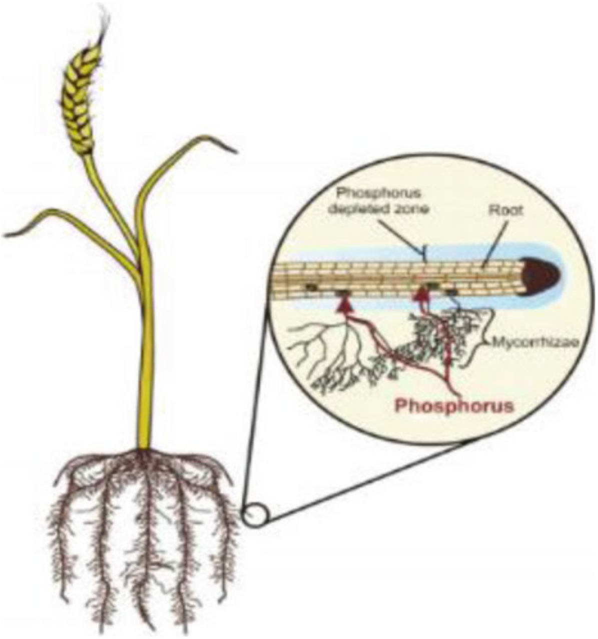


Fig. 4 Arbusculus structure expanding plant root surface. (Adopted from Bolduc and Hijri 2011)

contributes to organic matter content in the soil. AMF spore density was found to have a strong relationship to SOC, BRSP, and activity of soil acid phosphatase (Bai et al. 2009). Even the soil polluted by heavy metals shows a strong correlation of present AMF to GRSP, SOC and organic matter (Yang et al. 2017).

AMF is related to soil enzymes which are significant for the processes of organic matter mineralization (Zhou 1987). Soil enzyme activity may indicate microbial activity which is crucial for soil health and quality (Tarafdar and Marschner 1994). It was evidenced by a strong relationship of BRSP and soil enzymes, such as acid phosphatase and urease (Bai et al. 2009). Soil enzyme activity was found to be significantly increased by AMF inoculation, such as dehydrogenase, urease, saccharase, phosphatase by 6–225% (Qian et al. 2012). The fact is also confirmed by the study of (Wu et al. 2014b) who stated mycorrhiza significantly enhanced activities of β-glucosidase, peroxidase, phosphatase, and catalase, but suppressed the activity of polyphenol oxidase. The activity of hydrolytic enzymes is significantly related to glomalin, SOM, and soil structure (Gispert et al. 2013). It is interesting GRSP produced by AMF, and relevant soil enzymes are not dependent on external P content (Barto et al. 2010; Wang et al. 2015b). Soil enzyme activity was tested in the experiment using AMF inoculated plants under drought stress. Inoculated plants showed higher activity of peroxidase and catalase in both cases, with or without induced drought stress. The activity of polyphenol oxidase was affected neither by inoculation nor drought stress (Wu et al. 2008).

6 Role of Glomalin in Soil

Glomalin is not beneficial solely for fungi, but also for other soil organisms. It suggests the dual functionality of glomalin: physiological in the AMF mycelium and secondary in soil habitat (Purin and Rillig 2007).

6.1 Soil Aggregation and Carbon Storage

Soil resistant to water and wind erosion must be aggregated, stable, and with infiltration suitable for microorganisms and other organisms' growth (Bronick and Lal 2005). The soil fertility is based on its aggregation via: retaining nutrients near plant roots; sustained porosity enabling infiltration of water and air; carbon stock, protecting from carbonaceous compound decomposition; and diminishing erosion impact (Nichols and Wright 2004a). Well aggregated soil also prevents wind and water erosion as micro-aggregates are bound to macro-aggregates and thus cannot be easily washed by water or taken by the wind.

The factors affecting soil aggregation were analysed (Rillig and Steinberg 2002) and reported on the direct contribution of root length and glomalin to water-stable aggregates. Many authors pointed to the linkage between arbuscular mycorrhiza and stability of soil aggregates operating via glomalin (Rosier et al. 2006; Meena and Lal 2018; Wright et al. 1996) which is beneficial for AMF and host plant. Interestingly, glomalin effect was found to pose a much stronger effect compared to AMF hyphae. The many authors suggested that glomalin is significantly contributing to the stabilization of soil aggregates. Aggregate water stability and GRSP content in the environment strongly correlate (Bedini et al. 2009; Rillig 2004b; Rillig et al. 2010;

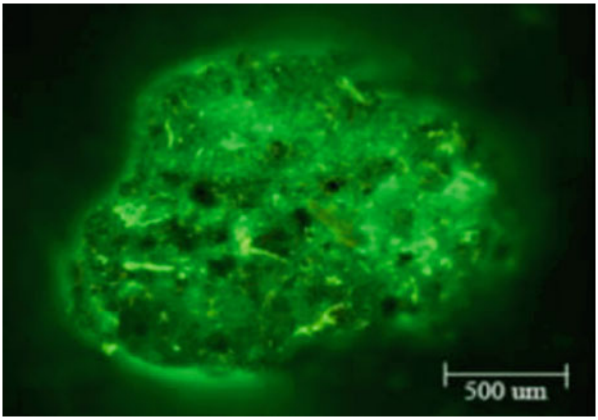


Fig. 5 Fluorescent visualization of glomalin in soil aggregate. (Adopted from Nichols et al. 2013)

Wright et al. 1998; Wu et al. 2014a; Driver et al. 2005) across broad spectra of soil types (Wright et al. 1998) and even in soil polluted by heavy metals (Yang et al. 2017). This might be the reason for GRSP persistence in soil (Gillespie et al. 2011).

Glomalin-related protein works as sticky glue joining soil particles together (Rillig and Mummey 2006). There is evidence that glomalin production is higher in non-aggregated to aggregated soil. Because hyphae of AMF grow better in aggregated soil, glomalin production is enhanced in site with impaired aggregate properties. It seems glomalin controls sub-optimal conditions for hyphae growth by aggregating soil particles into larger lumps (Rillig and Steinberg 2002). Polysaccharides of glomalin are sticky and keep smaller aggregates together. Iron creates bridges binding clay minerals and aliphatic amino acids. The complexes of organic (glomalin or humin) and mineral substances (clay) form a hydrophobic layer which protects soil from erosion by water and wind (Nichols and Wright 2004a). Structure of glomalin-bounded aggregate can be seen in Fig. 5 using fluorescent visualization of glomalin.

AMF and their exudates (including GRSP) can decrease the permeability of soil surface by increasing its hydrophobicity which stabilizes soil aggregates. The theory of aggregation ability may be supported by the discovered homology with HSP60 (Gadkar and Rillig 2006) as it plays the primary role in cell adherence (Hennequin et al. 2001). Aggregation is also a result of hyphae mediating stability (Tisdall et al. 1997). Their structure resembles “a flexible string bag” releasing GRSP and showing plasticity (Graf and Frei 2013). Aggregate stability is also promoted by fine plant roots (Tisdall and Oades 1979). Expanded system of roots provides more chances for AMF colonization, thus greater hyphae growth and more GRSP exudates affecting aggregate stability (Kohler-Milleret et al. 2013). The aggregate stability may also be enhanced by substances called hydrophobins which are released by AMF (Rillig and Mummey 2006).

Nevertheless, it is necessary to note that the correlation between soil aggregates stability and glomalin content is curvilinear. It means there is a point of saturation of no further increase in water aggregate stability (Rillig 2004b). The phenomena may be caused by the fact that all pores are already filled with glomalin. Aggregation stability is caused even by recalcitrance and long-term turnover of glomalin (Varma and Podila 2013).

However, some studies doubt whether aggregate stability is affected by glomalin (Purin and Rillig 2007). There was investigated a negative correlation between soil aggregation and AMF-mediated glomalin as the main cause of the soil aggregate stability (Rillig et al. 2003b). The stability was motivated mainly by carbonate concretions in Mediterranean steppes. Treated pine forestland with nitrogen addition within two years, causing an increase in GRSP and SOC did not affect aggregate stability (Sun et al. 2018). The authors assumed that aggregate stability formation is a long-termed process and depends on binding agents. Nevertheless, all the studies are based on macro-aggregates, and there is nothing known on micro-aggregates and related effects of glomalin. Furthermore, the contribution of some other factors, such as other microorganisms, could be involved in aggregates stabilization increase. Finally, glomalin is only a part of an organic substances pool. Thus it is complicated to predict their relation to the glomalin effect on aggregation (Varma and Podila 2013).

6.2 Resistance to Abiotic Stress

AMF reacts to abiotic stress differently. Their diversity and abundance are usually higher at non-disturbed sites. Polluted or sites with various abiotic stress are characteristic for lower AMF species richness with the prevalence of *Glomeraceae*. Even though AMF are sensitive to abiotic stress, some species have developed several mechanisms to defend against various stresses. The mechanisms involve antioxidant system, membrane lipid transformation or, e.g. sequestration processed by glomalin (Lenoir et al. 2016). AMF and GRSP can also improve the properties of soil and plants under various stresses, e.g. drought (Chi et al. 2018; Zou et al. 2013), salinity (Nichols 2008; Ibrahim 2010), extreme temperatures, nutrient deficiency, heavy metals (Li et al. 2015), organic compounds contaminations (Joner and Leyval 2001), and others (Gao et al. 2019).

6.2.1 Water Stress

The contribution of glomalin to reduce water loss is unknown as the results of the studies are inconsistent. Glomalin may cause reduced evaporation of water during drought (Gao et al. 2019) as it creates a polymeric hydrophobic surface of soil aggregates avoiding water loss (Nichols 2008) which might be related to the ability of glomalin to decrease the natural decomposition of water-soluble soil aggregates (Scott 1998; Thomas et al. 1993). AMF affected water retention positively through the glomalin effect in the study of Wu et al. (2008). On the other hand, investigated water repellence was not correlated to the glomalin presence, suggesting hydrophobicity is rather caused by AMF hyphae forming string-bag like structure holding particles together (Miller and Jastrow 2000). BRSP concentration was weakly increased by drought stress without significant differences (Wu et al.

2008). However, soil water deficiency-induced total GRSP and easily extractable GRSP production together with a water-stable aggregate of a size larger than 0.25 mm (Zou et al. 2014). Soil water repellence is probably a result of more factors and more hydrophobic substances released by plants, roots, and microorganisms (Hallett et al. 2003). Such a mixture of soil hydrophobic substances can behave differently at various moisture conditions (Dekker et al. 2001). When soil is wet, hydrophilic parts of the substances are not bound, and such soil is strongly hydrophilic. In case of moisture drop to some level, hydrophilic groups bond tightly together, exposing the hydrophobic part of the substance covering soil aggregates. It leads to the enhancement of water repellence (Dekker et al. 2001; Hallett et al. 2003). The effect is known as dual surface hydrophobicity (Morales et al. 2010), see Fig. 6.

6.2.2 Pollution by Heavy Metals

The AMF symbiosis brings benefit to plants, even in the polluted environment containing heavy metals. Fungi hyphae can accumulate the toxic elements in their cells to protect the roots of a host plant (Gonzalez-Chavez et al. 2002). GRSP is a factor affecting toxic elements in soil (Gao et al. 2019), e.g. by buffering and binding capacity (Wang et al. 2019), ability to stabilize or reduce the availability of toxic metals for host plants or microorganisms (Rillig 2004b). The topics are discussed more in detail in the following text devoted to soil remediation.

6.2.3 High Temperature

Despite the fact glomalin is tolerant to high temperature, unlike other proteins, the study applying different very high laboratory temperatures on different soil characteristics done (Lozano et al. 2016) discovered glomalin to be sensitive to fire. Therefore, the authors suggested that glomalin is a suitable indicator of fire severity. The findings are reported by other authors (Sharifi et al. 2018; Wuest et al. 2005). However, the correlation between fire and the glomalin concentration was not found (Knorr et al. 2003).

6.3 Biotic Stress

The hyphae protect plants against pathogens. It has been found that fungi and the plants have a system for communication. In the presence of a pathogen, the plant is warned early by the fungus and can release root exudates stimulating the growth of antagonistic microorganisms to the pathogens (Borowicz 2001). Glomalin has possibly originated as a coating of hyphae protecting from water and nutrients loss before they reach the roots of the host plants and as a protection from adverse microorganisms (Nichols 2008). However, there are theories linking glomalin production to AMF grazing stress caused by another soil biota. Glomalin production could be triggered by suboptimal conditions of mycelium growth in *Glomus intraradices* (Hammer and Rillig 2011). The experiment used fungus, which can clip AMF hyphae. The stress-induced by clipping has motivated AMF to increase

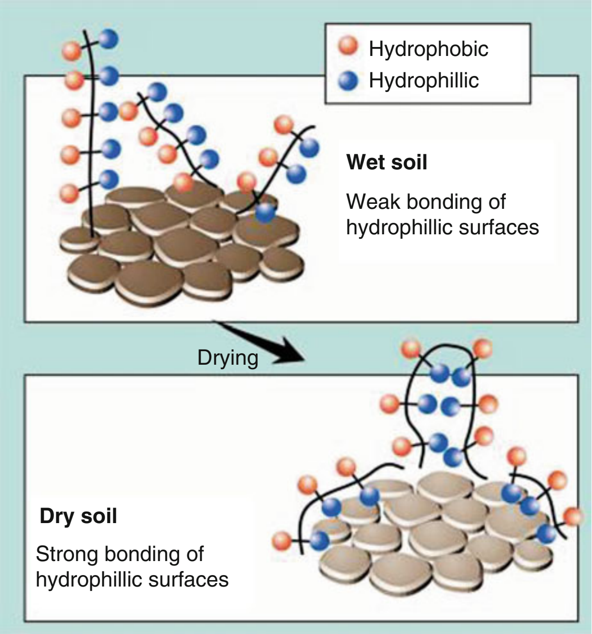


Fig. 6 Dual surface hydrophobicity of substances bound to soil particles. (Adopted from Hallett 2007)

glomalin production. This suggests glomalin is involved in defence from the grazing stress.

The study of Purin and Rillig (2007) hypothesized that glomalin might reduce the palatability of AMF in comparison to other soil fungi for microarthropods based on the study of Klironomos and Kendrick (1996) who also have confirmed that narrower hyphae further from plant roots are preferred for grazing. This theory supports the hypothesis of stress/inducible glomalin production and consensus with findings of another study (Driver et al. 2005) which found 80% of glomalin stock in hyphae and by the high degree of HSP60 and glomalin homology (Gadkar and Rillig 2006).

6.4 Glomalin Turnover and Recalcitrance

Chemically, it is clear that glomalin belongs to a group of glycoproteins produced by hyphae and AMF spores. The results suggested that it is hydrophobic, thermally stable and recalcitrant, which may be the reason for its relatively late discovery (Sousa et al. 2012a). The extent of recalcitrance ability is given by the recalcitrance index, which is determined by a ratio of alkyl and aromatic C to O-alkyl, carbonyl and carboxyl C (Ostertag et al. 2008). Zhang et al. (2017) investigated the recalcitrance index in the forest in a stage of natural succession (from 20–145%).

Based on C_{14} analysis, (Rillig et al. 2001a) estimated the average turnover time of glomalin for 6–42 years in the environment. Miller and Kling (2000), on the other hand, estimated the range to only 2.6–3.8 years. One possible explanation for this disparity may be that the AMF settles two functionally distinct sites: roots and soil. It is also one of the possible reasons for problematic assessment of AMF flows or time of environmental persistence as recognized by different authors (Miller and Kling 2000; Staddon 2003; Steinberg and Rillig 2003; Zhu and Miller 2003). Bonded organic carbon found in the clay fraction (organo-mineral complexes) shows a similar persistence time (Rillig et al. 2001b), which may indicate protection of glomalin from degradation by binding to clay minerals in soil (Lobe et al. 2001). Relatively slow glomalin decomposition can cause accumulation of the glomalin up to high concentration (Treseder and Turner 2007). Another interesting study (Knorr et al. 2003) found out a faster BRSP turnover in the forest compared to agricultural land. Treseder and Turner (2007) considered that soil microorganisms use a relatively high amount of N in glomalin as a source of nitrogen. Thus, the mineralization may be faster in soil with lower fertility where N is limited. The second theory is that there may be differences in glomalin chemical structure varying upon different ecosystems causing variable decomposition rate.

7 Glomalin Locking Carbon Stabilization and Sequestration

SOC pool is controlled by mechanisms of carbon sequestration and stabilization, which dramatically affects soil fertility (Goh 2004). Soil carbon can be found in two pools of SOM. One is easily degradable, indicated as particulate organic matter, and the other one is a heavy and recalcitrant fraction which is resistant to microbial decomposition, indicated as humic substances (Prasad et al. 2018).

AMF enhances carbon sequestration (Wang et al. 2009), but its production is substantially involved by the plant. The higher plant's nutrient demand leads to a higher amount of carbon supply provided by AMF. Most of the carbon is utilized to produce glomalin (Treseder and Turner 2007). The fungi may utilize up to 85% of soil carbon (Treseder and Allen 2000), Harris and Paul (1987) estimated that the rate of plant carbon transformation to the AMF can achieve 40–50% of photosynthetically assimilated carbon. Conservative estimate is 10–20% (Jakobsen et al. 2003) even in coastal marine systems (Wang et al. 2018). It was revealed that 27% of soil carbon is stored as glomalin which represents the main part of organic matter. Practically, glomalin encompasses one-third of the global carbon stock, while humic acid contributes to soil carbon by only 8%. Glomalin weight is 2–24x greater to humic acid (Wright and Nichols 2002). Glomalin is considered to be the largest pool of soil nitrogen and an essential reservoir of other elements under extractable SOM (Nichols and Wright 2004b). Glomalin concentration is responding to carbon fluxes and elevated carbon dioxide (Treseder and Turner 2007). Decomposition test with CO_2-C revealed glomalin is significantly correlated to active organic carbon stock in the soil in all the soil types and land-uses. It points to the fact that glomalin may be controlled the similar way as carbon in soil (Rillig et al. 2003b).

Soil sequesters carbon from the atmosphere, but it is accumulated only up to some level. Its potential to accumulate carbon is mainly based on the ability of carbon stabilization (Goh 2004). Carbon stabilization is tightly linked to many factors. One is soil aggregation and stability of soil aggregates. Stabilization of soil aggregates multiplies the significance of glomalin because the stabilization protects the inner part of carbonaceous substances from degradation (Wright 2000). Organic matter encapsulated in soil aggregates exerts suppressed decomposition (Prasad et al. 2018). Glomalin forms a hydrophobic layer on hyphae and keeps soil aggregates together, causing physical SOM/carbon stabilization inside (Rillig et al. 1999b). Alternatively, it is hypothesized that glomalin decelerates the natural disintegration of soil aggregates (Thomas et al. 1993).

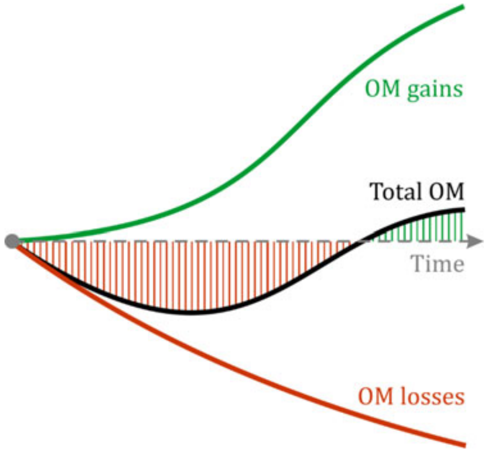
Soil carbon stock stability is enhanced even by the fact that when carbon is sequestered into glomalin, it becomes a part of the recalcitrant and hardly decomposable part of soil carbon stock. It should not be neglected that carbon in glomalin is stabilized as its turnover takes years depending on the site (Rillig et al. 2001b). Stubborn structure of glomalin-like proteins promotes sequestration of SOM, as Zhang et al. (2017) found that GRSP recalcitrance index is higher than the recalcitrance index of SOC in the environment of natural succession. In the same study, the authors suggest that GRSP contributes to SOC accumulation through retaining C and by recalcitrant composition prolonging C soil stock turnover.

Nowadays, it is not clear whether carbon contained in hyphae leads to SOC accumulation (Zhang et al. 2017). Some studies suggested AMF is conductive to SOC accumulation (Rillig 2004a; Zhu and Miller 2003), but some are claiming AMF is insignificant or even disadvantageous because results showed AMF accelerated SOM decomposition (Godbold et al. 2006; Hodge et al. 2001; Meena et al. 2020a; Tu et al. 2006). AMF may lead to SOC decomposition or even to soil carbon loss in the short term. Nevertheless, counteract was achieved by gaining C stock through a higher amount of recalcitrant compounds (Verbruggen et al. 2012), leading to long-term soil carbon stabilization. The dynamics of a short- and long-term carbonaceous compound stock can be seen in Fig. 7. However, AMF can accelerate the degradation of fresh residue, and it suppresses the degradation of former and aged SOC (Wei et al. 2019).

AMF is suggested to accelerate SOC accumulation at elevated carbon dioxide concentration (Antoninka et al. 2011; Meena et al. 2020b). It raises the question of whether AMF can buffer an increased amount of CO_2 within the global scale. The study of (Chen et al. 2012) poses a controversy attitude as their compelling short-term experiment carried out at an elevated concentration of nitrogen and CO_2 resulted in C pool loss caused by the accelerated rate of SOM decomposition. Nevertheless, the short-termed experiment could have detected a loss in C pool caused by accelerated decomposition, but in the long-term carbonaceous compound would instead increase as microorganisms and plants would be triggered by the decomposed compounds (Verbruggen et al. 2012), as explained in Fig. 7.

AMF must invest carbon to produce glomalin. Thus, higher carbon content enables AMF to produce higher glomalin stock. An elevated amount of carbon dioxide leads to the growth of glomalin concertation (Treseder and Turner 2007) and the growth of AMF in soil (Kasurinen et al. 1999). Thus, enhanced soil carbon accumulation presents a possibility to mitigate global climate change, especially

Fig. 7 Dynamic of gains and losses of organic matter. (Adopted from Verbruggen et al. 2012)



nowadays when degraded and nutrient-depleted soil could become a sink for an excessive amount of atmospheric carbon (Goh 2004).

In sandstone grassland, AMF reacted to elevated CO_2 level by increasing their hyphal length, but in serpentine grassland not (Rillig et al. 1999a). Under the same conditions, GRSP production was promoted in grassland (Rillig et al. 1999b), steppes (Rillig et al. 2003b) but not in the temperate forest (Garcia et al. 2007). The excessive content of carbon dioxide also caused glomalin gain in smaller soil aggregates (Rillig et al. 1999b). AMF reacted to the same condition in polluted soil by Pb and Cd. Sequestration of more heavy metals was detected as more GRSP was produced (Jia et al. 2016). The studies indicate there is a possibility that global change with its rising levels of CO_2 could increase soil aggregation and change soil structure, which could imply other studies of soil stabilization (Treseder and Turner 2007). Nevertheless, the effect of other inorganic substances on glomalin stock is not consistent.

8 Glomalin Management in Soil

8.1 Methods to Increase or Decrease Glomalin Level in Soils

The concentration of arbuscular mycorrhiza and hence glomalin is strongly dependent on vegetation cover and soil management (Martinez and Johnson 2010; Mirás-Avalos et al. 2011; Oehl et al. 2010). Higher glomalin concentration was detected in soils with vegetation ideally supplied with nutrients (Violi et al. 2007). Currently, many scientists are trying to increase the concentration of glomalin in the soil by inoculum of mycorrhizal fungi. *Glomus mosseae* was prosperous as an AMF inoculum in the experiment (Li et al. 2015). Importantly, the impulse that would trigger glomalin production by AMF hyphae has not been accurately elucidated yet (Rillig et al. 2001b). It is alluring that there was found a positive correlation of net primary

Table 3 Glomalin and soil aggregate stability affected by crop rotation (Wright and Anderson 2000)

Sample	Stability of 1–2 mm soil aggregates	Total glomalin (mg.g^{-1})	Immunoreactive total glomalin (mg.g^{-1})
W-F	11.6 (4.11)	2.3 (0.7)	0.57 (0.08)
W-C-M	12.6 (3.4)	2.9 (0.3)	0.56 (0.16)
W-C-M-F	12.0 (5.9)	2.5 (0.5)	0.61 (0.16)
W-C-F	11.5 (6.0)	2.4 (0.4)	0.62 (0.12)
W-S-F	7.4 (3.5)	2.3 (0.4)	0.52 (0.08)
Crested wheatgrass	59.9 (19.9)	3.0 (1.5)	1.70 (1.34)
Triticale	7.3 (3.3)	1.5 (0.3)	0.41 (0.08)

W – wheat; C – corn, M – proso millet, S – sunflower, F – fallow; mean and standard deviation are in parentheses

production and glomalin stock, but not with AMF abundance (Treseder and Turner 2007).

The studies suggested a no-tillage system is better to increase in GRSP or AMF colonization in the soil as conventional tillage mechanically disrupts a network of hyphae. The experiment comparing no-tillage to conventional tillage soil management observed positive results at the length of hyphae, GRSP content, water-stable aggregates, total mycelium and total carbon when applying a no-tillage system (Curaqueo et al. 2010; Filho et al. 2002). Soil management was reported to affect glomalin concentration (Rillig 2004b). Effect of different agriculture management on soil aggregation showed the best output within no-tillage management in topsoil layer 0–20 cm (Filho et al. 2002). Contrarily, the soil with physical disruption of soil structure, e.g. by tillage, was investigated with lower glomalin content in several studies (Borie et al. 2000; Sharifi et al. 2018; Wright and Anderson 2000; Wright et al. 1999). The relation of glomalin concentration to grazing has not yet been statistically demonstrated (Franzluebbers et al. 2000). These findings suggest that GRSP production is highly sensitive to agro-technical interventions even at their short-term application (Rillig 2004b). Generally, application of lime, mineral fertilizers or pesticides and similar approaches of the agricultural management alter the soil environment and affects soil organisms (Prasad et al. 2018).

Another parameter affecting glomalin concentrations in the soil is the crop rotation (Wright and Anderson 2000), see Table 3. Based on this, the best results were achieved with crop rotation wheat–corn–millet with the application of no-tillage soil management. On the other hand, aggregation of soil was not affected by crop rotation (Filho et al. 2002).

After the application of organic material, in particular manure, liquid manure or compost increased content of glomalin is usually observed (Curaqueo et al. 2011; Oehl et al. 2004; Valarini et al. 2009). Several doses of compost were used, and the increase in glomalin content was proportional to the dose of compost (Valarini et al. 2009). The same effect was shown even on the combination of chemical fertilizer and straw in rice cultivation (Nie et al. 2007).

8.2 Effect of GRSP Treatment on Crops

Some studies deal with the treatment using exogenous easily extractable GRSP. They seem to have a promising effect on fertility and structure of the soil, plant growth and their tolerance to stress (Gao et al. 2019). Different types of treatment using easily extractable GRSP have found a positive effect on the increase in biomass, dry weight, the activity of soil enzymes, length of roots or photosynthesis intensity (Wang et al. 2016; Wu et al. 2015; Chi et al. 2018).

Soil inoculated with two AMF species was detected with elevated SOC, total and extractable GRSP in the rhizosphere. Its impact was seen in limited fungi presence and no affection of soil bacteria (Zhang et al. 2019). The authors reported that GRSP and SOC were highly related to the limited richness of fungi species. AMF inoculation also improved plant biomass, carbohydrates, BRSP, and water-stable aggregates (Wu et al. 2008).

8.3 Potential Role of Glomalin in Soil Sustainability

With all the mentioned characteristics, AMF and their product glomalin contribute to soil sustainability. AMF may positively affect soil physical and chemical properties (Gao et al. 2019), such as improved stability of aggregates (Bedini et al. 2009; Rillig et al. 2010; Wright et al. 1998; Wu et al. 2014a), reduced water loss (Zou et al. 2013), resistance to biotic or abiotic stress (Amiri et al. 2016; Ibrahim 2010; Li et al. 2015; Nichols 2008), and the soil enrichment with SOM (Verbruggen et al. 2012). Moreover, it subsidizes plants with organic substances (Quilambo 2003; Treseder and Turner 2007) which may significantly affect crop productivity (Adesemoye et al. 2008). AMF effect is a complex system improving soil health and quality and shall not be neglected at any of the agricultural intervention.

Soil sustainability may be promoted using the system of integrated nutrient management which aims to join added and natural sources for plants efficiently to maintain yield and productivity (Gruhn et al. 2000). In such systems, AMF could play a significant role as they are capable of enriching the soil with nutrients without any other intervention. AMF has been used in the experiment of (Adesemoye et al. 2008), resulting in improved nutrient and yield properties. The experiment combining the plant growth-promoting rhizobacteria with AMF brought promising results as biofertilizers and increased uptake of N, P and K nutrients by plants.

8.4 Glomalin Remediating Polluted Soil

Glomalin can sequester potentially toxic elements, and thus it may be contributing to phytostabilization in polluted soil (González-Chávez et al. 2004; Yang et al. 2017). AMF inoculation was carried out to reclaim soil in a mine resulting in significant improvement of the soil state (Qian et al. 2012).

Glomalin is able to sequester heavy metals, in particular Cu, Pb and Zn (González-Chávez et al. 2004; Chern et al. 2007; Vodnik et al. 2008). One hundred eighty-eight mg of Pb and 4.8 mg of Cu can be adsorbed by 1 g of glomalin (Cornejo et al. 2008; Chern et al. 2007). Different results were mentioned by González-Chávez et al. (2004) who tested hyphae of *Gigaspora margarita* and found even 28 mg of Cu per gram of glomalin. In mangrove wetlands, an investigation found that GRSP immobilized and sequestered heavy metals which reduced their mobility (Wang et al. 2019). The authors reported on the fact that glomalin sequesters Cu through reversible reaction and possibly via complexes (González-Chávez et al. 2004). AMF produces excessive amounts of glomalin to affect the bioavailability of copper to eliminate its toxicity to soil biota. It suggests they provoked glomalin production, as protection from Cu-toxicity, could be a primary function of the glomalin (Ferrol et al. 2009; Lenoir et al. 2016). In addition, some authors reported even some affinity of glomalin to aluminium (Aguilera et al. 2011; Seguel et al. 2016).

However, all heavy metals do not involve AMF the same way. Pb was found to be significantly more toxic to AMF, causing a reduction in the content of SOM, SOC, and GRSP, compared to Zn (Yang et al. 2017). Despite the fact, glomalin binds Cd and Pb, the overall effect on heavy metals is affected by other factors. The experiment led by Wu et al. (2014c) showed that the amount of sequestered Cd and Pb by glomalin was negligible in comparison to the sorption capacity of SOM.

9 Conclusion and Perspective

Despite considerable blank space in the understanding of GRSP and glomalin, future work can be pointed to enlarge the knowledge on soil structure, and its quality, further applicable soil management as well as new biotechnology approaches in modern agriculture (Rillig 2004a). There are still unknowns and vague information on glomalin structure and its constituents. Optimization of glomalin extraction is needed as the current methods offer results contaminated with impurities obstructing glomalin identification, such as tannins. The exact structure of glomalin is complicated as its extraction is harsh and may eliminate heat-labile proteins. Thus, new and less laborious methods of its extraction led under more moderate conditions would help the further investigation. Another obstacle to uncovering the structure of glomalin presents the fact there is a possibility glomalin can have different compositions depending on the environment. There is even a question of glomalin structure reveal ability, as some facts point to its changeable composition.

There is still missing evidence on the primary function of glomalin as it has not been discovered. The studies provide variable suggestions. Nevertheless, they agree that glomalin production is advantageous for AMF survival. The functions encompass better soil aggregation, protection from metals toxicity, protection from fungi grazers or generally higher ability to withstand impaired living conditions.

Another topic, which offers many gaps in understanding, is soil structure and glomalin concentration under elevated carbon dioxide levels, as there is a hypothesis of glomalin ability to buffer carbon dioxide excess. There are no known mechanisms and patterns of glomalin reaction and contribution to the soil which can be expected under the predicted climate change scenario. Glomalin production and decomposition shall also be investigated as the studies could provide more knowledge on its function for AMF. It could also shed some light on the prediction of glomalin content in the ecosystems affected by climate change. Currently, enhanced soil carbon accumulation presents a possibility to mitigate greenhouse gasses as degraded soil could become a sink for an excessive amount of atmospheric carbon.

Finally, soil sustainability may be achieved by the system of integrated nutrient management which aims to join added and natural sources for plants with efficiency to maintain yield and productivity. In such manner of agriculture management, there is a vast space for new biotechnological procedures comprising AMF and GRSP.

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Clay Mineralogy: Soil Carbon Stabilization and Organic Matter Interaction

Sneha Rani

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Abstract

In recent time, concerns are rising related to climate change, and mitigation measure such as soil has caught attention for the research community as a reservoir for storage of atmospheric carbon dioxide (CO_2). The soil organic carbon (SOC) stabilization mechanisms have recently received a lot of focus because of its significance in governing the global carbon (C) cycle. The aim of the present chapter lies in reviewing the existing understanding on soil organic matter (SOM) dynamics with particular mention toward the contribution of clay mineralogy in retention as well as the stabilization of organic C in the soil. Thorough knowledge of the SOC stabilization mechanisms would assist in implementing optimal management practices for storage of SOC, enhancing the soil structure, and lastly mitigating the emissions of greenhouse gases. In this chapter, the relationships existing between SOC dynamics with its sources as well as sinks, aspects controlling SOC sequestration, and several mechanisms involved in the process of SOC stabilization are discussed. The studies related to soil examination, management, and environmental factors that affect the SOC stabilization with a particular mention to the clay mineralogy are provided.

Keywords

Soil organic matter · SOC sequestration · Clay minerals · Stabilization

Abbreviations

SOC	Soil organic carbon
SOM	Soil organic matter
UNFCCC	United Nations Framework Convention on Climate Change
IPCC	Intergovernmental Panel on Climate Change
GHGs	Greenhouse gases
CO_2	Carbon dioxide
CH_4	Methane
SDG	Sustainable development goals
AMF	Arbuscular mycorrhizal fungi
CEC	Cation exchange capacity
DOC	Dissolved organic carbon
SSA	Specific surface area
OH	Hydroxyl
N_2O	Nitrous oxide

1 Introduction

The term “climate change” was coined by the United Nations Framework Convention on Climate Change (UNFCCC) that signifies the change in climate which is as a result of the direct or indirect human activities tending to change the composition of atmosphere globally and also variation in climate as observed over considerable time periods. On the other hand, Intergovernmental Panel on Climate Change (IPCC) explains the climate change as a certain kind of change in the climate with time, which may be due to the natural variation or involvement of human activity (IPCC 2001). This variation in natural processes and human activities are causing the release of greenhouse gases (GHGs) – comprising of methane (CH_4), C dioxide (CO_2), and nitrous oxide (N_2O). Increase in the concentration of these GHGs is leading to a rapid increase in temperature globally. With respect to IPCC (2007), the earth’s surface has been warmed by 0.74 °C since 1990 due to the rise in GHG emissions. This has raised a lot of discussion around climate change and global warming globally (Lal 2004). GHG level has increased rapidly since the preindustrial revolution ranging from 280 ppm to 404 ppm and is being predicted to reach 550 ppm by 2050. With a faster rate of increase, this level might reach early by 2035 (Stern 2007). Emission of CO_2 among the rest of GHGs is regarded as a key contributor toward global warming. The rise in CO_2 emissions is major as a result of the exploitation of fossil fuels as well as the land-use change to a certain extent. In the current scenario of climate change, the land-use degradation and loss of flora and fauna, soil around the world has turned into one of the vulnerable resources. Soils are the source of C reservoir comprising of higher amounts of C than the atmosphere and terrestrial flora combined together. C tends to enter the soil as organic matter formed from the biodiversity (or flora and fauna) and is available in the soil for longer periods. This soil organic carbon (SOC) is emitted as CO_2 back into the atmosphere or released during soil erosion or getting washed as dissolved organic C in water bodies. With proper management, soils around the world can be utilized as pools of CO_2 rather than as a source.

The SOC is an essential component of organic matter present in the soil. The soil C largely contains plant matter, but a small amount is also derived from mineral matter. SOC largely determines the health of the soil and contributes toward mitigation and adaptation to climate change and assists in achieving sustainable development goals (SDG). SOC further enhances the stability of soil structure by helping the formation of aggregate that, along with the presence of porosity, ensures adequate aeration and water penetration to promote the growth of plants. The optimum SOC supports the water infiltration of soil, leading to a clean water supply. With the enhanced mineralization of SOC, soil acts as an evident source of GHG emissions released into the atmosphere. In the global context, SOC comprises of different areas of the bright and hot-spots. The hot-spots exhibit extreme sensitivity toward climate change and as a result of high SOC are easily susceptible to becoming a source of GHG emissions. On the other hand, bright spots comprise of huge landmass having lower SOC content that can act as promising sites for CO_2 sequestration.

Globally, SOCs are identified as one of the biggest C pools (Lützow and Kögel-Knabner 2009). Pools are a sink of C that store huge amounts in comparison to its release, while sources of C tend to discharge more than store. Aquatic systems such as oceans, soils, and vegetation are the major planetary C pools. Until now, oceans including aquatic systems are the largest C pool with an estimate of 38000 Gt, after which the soils having an estimate of 2500 Gt and least is vegetation amounting to 650 Gt. Around the world, total C pools in soils in the total landmass (eliminating C present in charcoal and litter) is estimated to be 2157–2293 Gt in the upper layer of soil ranging up to 200 m. It is estimated that SOC in the higher layers of 30 cm amounts to 684–724 Gt, 100 cm amounts to 1462–1548 Gt, and estimate of 2376–2456 Gt for 200 cm (Batjes 1996).

Generally, at appropriate conditions, fauna in soil metabolizes the C compounds adding some amount of C from its biomass, whereas the remaining amount is released in the form of CO_2 into the atmosphere or expelling back to the soil. As a result, a continued movement of C is occurring along the food chain of soil signifying the change in the form of C into various compounds or during its integration with new microorganisms. The C pools have been classified on the basis of duration of its presence in soil into three groups, namely; fast, slow, and stable pools (Jenkinson and Rayners 1977). In the fast pool, the SOC turns around and gradually moves back to the atmosphere that can span from some days to years. This C usually comprises of freshly included residues of plants and C compounds released from roots. The microbes present in soil mostly use the fast pool as it generates larger amounts of CO_2. While slow pool comprises of plant left-overs (that are highly processed), microbial residues (from fast pool), and molecules of C (untouched by microbes due to the biochemical/physical processes of soil). The slow pools have mean residence time which ranges from several years to decades controlled due to various soil properties (such as climate, management, and texture). On the other hand, the stable pool is resilient to instabilities, and change is minimal in the range of centuries to millenniums. It comprises of hummus (C compound assembly, i.e., highly resilient to degradation) and soil C is uninfluenced by microbial degradation (Six et al. 2002). The sizes of these pools are different for various types of soils. Overall, the sizes of fast and slow pools exhibit sensitivity toward management, while stable is usually constant. Similarly, the SOM can be categorized into active and passive pools on the basis of its entire degradation as well as residence time (time of turnover) of different products available in the soil (Gougoulias et al. 2014). The turnover time of the active pool ranges from months to some years, while, in the case of passive pools, the turnover extends until thousands of years. SOM range between 55 and 60% by mass and in the majority of soils, this type of C is composed of almost all the C and known as SOC (excluding the site of inorganic matter occurrence) (Pennock et al. 2015). Generally, the fraction of active SOC to the entire SOC affects C sequestration in soil and health of soil (Blair et al. 1995). The active C proportion is identified as essential physical and chemical factors of the soil. Basically, the stable component of the SOC is contributed to the soil's cation exchange capacity (nutrient holding capacity). Moreover, as a result of the slow decomposition of this C, it can be useful in SOC sequestration for the longer term.

2 Clay Mineralogy

Several definitions are available for clay minerals due to the complexity in structure. The clay minerals are silicate layers formed due to the chemical weathering products of different silicate minerals at the surface of earth. Clay minerals are mostly found in shales which are commonly available sedimentary rocks. Clay minerals tend to hold moisture and dissolved nutrients of plants weathered from various minerals as a result of adsorption, which is a surface phenomenon. The clay minerals appear to have a similar chemical composition as that of mica. Clay minerals are flaky in shape with uneven edges and one side is smooth and its fine-grained property differentiates it from mica that is microscopic. Clay minerals denote the class of phyllosilicates that are hydrated which form fine-grained particles of sediments, rock, and soils. Another definition states that clay minerals are phyllosilicate minerals that provide plastic property to clays that tend to strengthen during drying or firing (Guggenheim and Martin 1995). One of the definitions also states that clay minerals can be phyllosilicates/non-phyllosilicates and natural/synthetic. Phyllosilicate structures are based on T (tetrahedral) and O (octahedral) sheets which may tend to condense in 1:1 or 2:1 fraction, thereby forming anisotropic layers (TO/TOT) (Churchman and Lowe 2012). Clay minerals have characteristic properties that are: layered structure having per unit dimensions in nanometer scale, anisotropic particles or layers, different types of surfaces exist (planar/external, edged and internal/interlayer surfaces), modification of external and internal surfaces by grafting or ion exchange or adsorption, plastic property and lastly as discussed above hardening by firing/drying (Annabi-Bergaya et al. 1979). In some studies, the clay minerals are also associated with smectite due to various properties, such as: colloidal-sized particles, higher specific surface area, higher extent of disorder in layered stacking, medium layer charge, and anion exchange capacity.

Clay minerals are divided into two types based on the ability to adsorb water molecules as *swelling* and *non-swelling*. The smectites are the swelling type of clay minerals and this swelling property is typical of clays (Dixon 1991; Pal et al. 2009). The composition along with structure are other important properties of clays used for classifying clay minerals. The clay minerals illite, smectite, kaolinite, chlorite, and needle-like shape sepiolite-palygorskites are some predominant clay minerals abundantly available globally. In the latter part of the chapter, the critical role of clay minerals in soil in C sequestration has been discussed.

2.1 Montmorillonite

These minerals are hydrated and with a rise in temperature as well as pressure at the time of burial, water is expelled from interlayers. The interstitial solutions (primarily concentrated) obtained during diagenesis releases cation that replaces water molecules present in between layers. This is a reaction irreversible in nature that generates chlorite (14-A) or illite (lo-A) minerals, which undergo structures that are mixed layers. The absence of montmorillonite is commonly marked as burial formations. Montmorillonite is a 2:1 clay mineral having larger surface areas and high CEC (Greenland 1965).

2.2 Kaolinite

The kaolinite is associated with the surface of the earth's crust which is also its zone of formation and categorized by aluminum in hexacoordination (De Lapparent 1941). It provides paleographic markers in older sediments. When undergoing diagenesis, kaolinite exhibits sensitivity to geochemical conditions, show stability in a stable environment and alkalinity in unstable environment. On the other hand, during the rise in temperature with burial results in damage at the earliest or with time. Kaolinite is unavailable in the transitional stage to anchizone (metamorphism). In acidic conditions, nacrite and dickite can only be observed. In Fig. 1, back-scattered electron images of sedimentary rocks are shown that comprises of kaolinite (clay mineral), organic matter, and non-clay minerals.

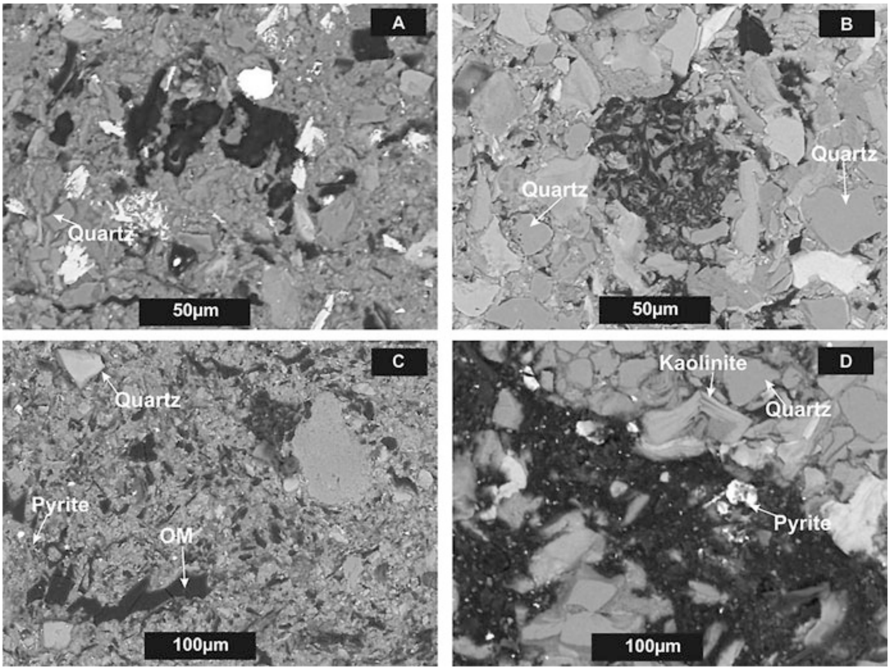

Fig. 1 Back-scattered electron images of sedimentary rock showing: (**a**) and (**b**) non-clay minerals, (**c**) organic matter, and (**d**) kaolinite as clay mineral

2.3 Mixed Layer

This type of minerals occurs at intermediate stages through weathering causing degradation and also at the time of aggradation which is due to deep diagenesis. The aggradation stage is due to the inclusion of definite cations obtained from the interstitial solutions, and restructuring inside the lattice. The illites are produced by two ways which are sodium and potassium paths. Then micas pass through regularly mixed-layer type of allevardite-rectorite and the magnesium path generates chlorites that pass by a mixed layer of corrensite type. The mixed layers of these types stay stable metamorphism boundary (Muffler and White 1969).

2.4 Illite

These mica type of clay minerals form an extremely heterogeneous group in the soil (that are subjected to hard diagenesis). Illites are composed of particles which are diverse in origin and during burial the diversity lowers. During deep diagenesis and metamorphism, illite with crystallographic parameters is considerably defined well which serves as a recrystallization scale (zoneographic index). This changes the morphology of the particles and polymorphic types (1 M and 1 Md) being replaced by the 2M type (Yoder and Eugster 1954).

2.5 Mica

At low-grade metamorphism stage, petrographers call it sericites. It is different from original micas with weak charged layer, i.e., smaller than 0.9 in half-cell and is usually composed of sodium (paragonites and paragonitic muscovites). As a result of replacement of the aluminum with Mg and Fe^{2+}, octahedral charge (0 for muscovite) is normally high.

2.6 Chlorite

The chlorite means are less popularly known clay minerals. During the early diagenesis, detrital constituents can get aggraded into chlorite by subjecting it to a stage of mixed-layer corrensite. The substantial growth in chlorite is noticed during late diagenesis and metamorphism. Chlorite and illite slates provide space to chlorite and sericite schists (Whitehouse and Mccarter 1958).

3 Clay Diagenesis and Structure of Clay Minerals

Clays are an essential component of earth's surface and the *weathering* process generates huge amounts of clay material. The process of sedimentation and its burial alters the clay characteristics and transforms clays into different clays. Clay sedimentation mostly occurs in marine environments (lake/ocean) and alteration of clay mineralogy takes place just after deposition, i.e., interface of sediment-water (Eberl 1984). During the preliminary sedimentary burial stage, the sediment concentrates to dissolve particles in an aqueous solution. Eventually, resulting in the change of chemical equilibria and in this sedimentary environment, clays have higher residence time compared to the process of weathering. The origin of clay mineral groups is unique in a sedimentary environment and its reactions are oxide-clay and clay-clay. The formation of new minerals is greatly controlled by the surrounding oxidation potential. The organic matter plays a critical role in controlling the oxidation state of silicates (Arndt et al. 2013).

On the other hand, in deep-sea environments, the rocks and marine water interact to impact a particular weathering type or diagenesis. For example, basalts (that are predominant in oceanic-floor environment) are found to hydrolyze leading to the formation of clay on the surface. Clay groups formed are specific to this environment of eruptive rocks (glassy in nature) and could also be useful in depicting origin and presence in deep-sea environments (Kerr 1952). In case of burial diagenesis, during the burial of clays available in sediments, there is a change in the ratio of water-rock and clays dominate in the chemical equilibria of solution and solid. Under such conditions, gradual modifications release new minerals from the minerals present in sediments that are metastable. With subsequent burial, temperature of sediment varies that alters mineral stability that in turn produces new clay types in such an environment. In conditions of high temperature with further burial, clay minerals come to a recrystallization state, popularly known as metamorphism (Miyashiro 2012). This stage explains thermodynamic conditions dependent on the temperature reached and duration of time for clays to get affected. These metamorphic conditions tend to coarsen the minerals by the growth of crystals as well as the creation of new silicate type of minerals and sheets of silicates. Even though the structural and chemical properties of mineral grains from metamorphosis are similar to clay the size is too big to be termed as clay. Moreover, its crystallographic composition is not analogous to lower temperature and fine-grained clays. Hydrothermal processes (that involve interaction between water and rock in the temperature of 100–250 °C) are responsible for the production of some amount of high-grade clay materials with application in different stages in industries. In the hydrothermal alteration process, dissolution as well as deposition occurs. It is an important process where the presence of clay minerals is slightly noticed due to rock alterations as a result of occurrence of huge amounts of heated water (Utada 1980). This type of weathering process (higher water-rock ratio) is achieved at temperatures greater than 50 °C. In symmetry, majority of ore mineralization at higher depths is associated with clay/clay-type mineral formation. The analogous method is connected with placement of magma of basaltic-type under ocean floor that leads to the formation of numerous clay minerals and also accompanied by loss of several elements from basalts.

The diagenesis of clay minerals undergoes various stages ranging from early diagenesis, middle diagenesis, late diagenesis, and metagenesis (Muller 1967). The early diagenesis is a stage where burial occurs at shallow depth and clay minerals are stable in this stage. However, some clay minerals are subjected to aggradation as a result of Na, K, and Mg adsorption (forming different mixed layers) (Alekseeva 2011; Bolan et al. 1999; Churchman and Lowe 2012) and few are newly formed such as montmorillonites. In middle diagenesis stage, also called as "early catagenesis" takes place at higher burial depths and the sediments in this stage turn into the compact. During this stage, sediment loses 50% (minimum) of the connate water. The porosity is higher and few detrital minerals like biotite is unstable. The entire clay minerals in this stage continue to remain stable but because of circulation in interstices, several varieties of replacement are occurring simultaneously. In this stage kaolinite and montmorillonite undergoing dickitization and illitization respectively can also be observed. In case of late diagenesis, the temperature is higher than 100 °C, the pressure rises and leading to porosity turning to be extremely weak. The uneven mixed layers and montmorillonites vanish. When subjected to an acidic environment, recrystallization of kaolinite takes place turning into dickite. These kinds of transitions are irreversible in nature. Lastly, the metagenesis or anchizone is a transitional stage toward metamorphism occurring at a temperature around 200 °C (Kossovskaya and Shutov 1963). The only silicate sheets found are illite and chlorite. Nonetheless, other minerals such as dickite and pyrophyllite are found to be associated along with the allevardite. Crystallographic properties of the illite explain limitation of this zone, i.e., metamorphic epizone.

The phyllosilicates (i.e., clay minerals which are aluminosilicates, mostly the layered-lattice) (Pal et al. 2009), hydroxides, metal oxides, oxy-hydroxides (such as goethite, hematite), and aluminosilicates of short-range order (like imogolite, allophane) are the prime minerals available in soil contributing to the stabilization of organic matter. These minerals have organic molecules that have surface interaction property, i.e., controlled by different factors such as: (i) surface topography, size, and shape, (ii) type of surface charge (amount, polarity, and features), and (iii) degree to which particle aggregate.

3.1 Phyllosilicate or Layer Silicate Minerals

The phyllosilicates occur in soil with sizes smaller than 5μm that are really diverse. The phyllosilicates have a crystal structure that mainly governs its properties that arises the importance to understand its structure. Due to the variation in its layered structure, these kinds of silicate layer minerals have different properties, for example, CEC, water penetration, and specific surface area (Dixon 1991). These variations in properties can influence the SOC stabilization and also influence the physicochemical characteristics of soils (Hassink 1997). Let us consider, vermiculites and smectites (2:1 type and expanding) have a higher specific surface area (SSA), due to both higher CEC and smaller particle size, and that provides clay minerals with a greater adsorption capacity. The affinity of water toward smectite pores makes it swell (Dixon 1991; Pal et al. 2009). However, illites (2:1 type, nonexpanding) and kaolinites (1:1 type) usually have lower CEC, larger particle size, and smaller SSA compared to smectites (Churchman 2006; Dixon 1991). The soils are rich in montmorillonites and vermiculites (2:1 clay minerals) with a greater degree of C protection in the soil than kaolinites (1:1 clay minerals) because of greater CEC and SSA (Hassink 1997; Wattel-Koekkoek et al. 2001; Six et al. 2002). The kaolinite (1:1), vermiculite (2:1), and smectite are some of the common phyllosilicate type of minerals. Kaolinite with layer (1:1) type of structure comprises of the two sheets that is one octahedral as well as one tetrahedral and the apical oxygen ions of tetrahedral sheet is shared with octahedral sheet. The layer of 2:1 type of structure comprises of the octahedral sheet that is present in the middle of 2 tetrahedral sheets. The Si^{4+} ions present in tetrahedral sheets occupy the majority of tetrahedral and can be replaced with Al^{3+} ions. While, in octahedral sheets, divalent cations (Fe^{2+}/Mg^{2+}) or trivalent cations (Fe^{3+}, Al^{3+}) occupy the octahedral. In case of trihedral sheets, entire octahedral sites are occupied by trivalent cations, while for dioctahedral sheets divalent cations occupy 2 out of 3 octahedral sites and the last (3rd) site remains empty. The structure of tetrahedral sheets along with octahedral sheets is responsible for making free charged or negatively charged layer. In such structure, a cation is isomorphically substituted by a cation of low charge (like in octahedral sheets, Al3+ ions by Mg2+ ions) rendering a stable net negative charge in the clay layer. If at all these layers possess charge, cations balance this charge (Bolan et al. 1999; Alekseeva 2011; Churchman and Lowe 2012). The isomorphic substitutions are popular in 2:1 clay sheets resulting in a negative charge, i.e., permanent, while 1:1 silicate sheets are less popular. Both the 1:1 and 2:1 clay sheets contain varying charge that are consistent with surface charge produced by hydroxyl group reactions (protonation-deprotonation) at the surface. Phyllosilicate minerals also significantly contribute to silt and sand (Pal et al. 2009).

3.2 Secondary Minerals

The metal oxides contribute to influencing the soil properties and also are abundantly available in soils. Iron and aluminum oxides, hydroxides are commonly known as oxides that are reactive in nature, specifically in acidic or neutral soils. The formation and changes in metal oxides are strongly impacted by biomolecules (Huang et al. 2002). Fe oxide minerals are popularly known to impact the physical characteristics of soil (Tan 1982). The Fe oxides are adsorbed on the surface of kaolinite, with cementation effect, causing subsequent development in a higher aggregation of primary soil fractions that concrete and form crust (Baver 1963). All the iron oxides impart predominant color into the soil, i.e., available in small quantities and these iron oxides tend to form aggregates that are stable in form by cementing with other minerals. The iron oxides mostly are made up of stream of O as well as hydroxyl (OH) ions. Goethite (α-FeOOH) is the most common Fe oxide mineral found in soils and gives strong reddish-brown and brown color to the soils. Other iron oxide minerals such as hematite (α-Fe_2O_3) plus maghemite (γ-Fe_2O_3) impart pinkish to shiny red color. The structure of goethite is formed due to the close packing of O atoms that are in the form of hexagonal arrangement. Some other oxides tend to have a complex structural arrangements such as lepidocrocite (Tan 1982). As discussed above, the isomorphic substitution of aluminum and manganese ions with iron occurs frequently. Iron oxide concentration in soil ranges from 1 to 500 g/kg and due to thermodynamic stability of hematite and goethite minerals are usually present in an aerobic environment (Pal et al. 2009; Kampf et al. 2012). Several hydroxides, crystallographic oxides as well as oxyhydroxides of aluminum are also present in the soil. The gibbsite ($Al(OH)_3$) being a commonly available mineral in these types of soils and an important mineral constituent of oxisols and ultisols. The layer of gibbsite is made up of hydroxyl layers combined together with aluminum ions being octahedrally coordinated and Al^{3+} ions fill the 2/3rd of potential empty cathedral interstices. The OH groups of 1 layer are exactly opposite of OH group of the subsequent layer and are held strongly using hydrogen bonds (Tan 1982). The adsorption of aluminum oxides on heavy metals is higher because of greater surface area values that range from (100–220 m^2/g) (Kampf et al. 2012). Along with iron and aluminum oxides, gibbsite plays an integral part in the aggregation of soil but processes are unclear till now. The iron is accompanied with the clay minerals in the form of coating of oxides. Basically, the clay minerals have “-ve” charge, due to which oxides having positive charge is balanced that stabilizes clay fractions and it induces clay flocculation which protects SOM from microbial intervention (Churchman et al. 1993; Baldock and Skjemstad 2000; Favre et al. 2006).

4 Carbon Sequestration

C sequestration is the method by which CO_2 is captured from the atmosphere and stored in large natural pools permanently so that it does not escape back to the atmosphere. Likewise, SOC sequestration is the technique of capturing atmospheric C through plants or organic leftovers and storing them in the soil. While handling CO_2, SOC undergoes three different phases that are: (a) removing atmospheric CO_2 through photosynthesis of plants, (b) separating the C from CO_2 and then transferring to the plant biomass, and (c) transferring the C in plant biomass to SOC in the active pool. This active pool involves freshly included plant residues and gets easily decomposed by soil fauna, leading to CO_2 emissions that are released and returned to the atmosphere. Hence, the capture of CO_2 in the process of SOC sequestration should not be the ultimate motive rather retaining C in the slow pool of SOC. On the contrary, studies show that slow pool has minimal C sequestration potential as a result of its least resistance to variation (Kane 2015; Meena and Lal 2018). There are different methods of stabilizing freshly included C in the soil (Six et al. 2002, 2006; Kane 2015). In physical terms, C can be stabilized through isolation within micro- plus macro-aggregates where it does not get access to the organisms present in soil. While chemically, the C adsorption may occur through chemical bonds in the clay that resists C being consumed by organisms. Lastly biochemically, the C may tend to get synthesized again turning into a complex molecular structure thereby, preventing decomposition. These three processes are dependent on various factors such as biotic and non-biotic/abiotic that contribute to the efficiency of C stabilization in soil (Six et al. 2006; Kane 2015).

Soils tend to have a fixed capacity for C sequestration (Paustian et al. 2000). The soils of finer texture usually possess higher amounts of SOC compared to soils of coarser texture during the application of equivalent organic input amounts. An essential factor that promotes the SOC stability is the adsorption on to silt and clay particles. In general, the basic statement is that the mineral soil tends to have a maximum amount of SOC storage (i.e., in per unit volume) estimated by the silt ($<$20μm) and clay content. The study on tropical and temperate mineral soils help determine the correlation between SOC and soil texture, and also is useful in suggesting that the quantities of C can be linked with silt and clay. It was stated that as that the upper level for the organic inputs adsorption on to the silt and clay is reached, the application of extra organic matter on the soil does not cause an increase in C sequestration (Hassink 1997). Hassink (1997) further observed that a close correlation exists between the fraction of the primary particles ($<$20μm) present in soils and the associated SOC with this proportion at the top of 10 cm. The quantity of SOC in the $>$20μm proportion was not related with the texture, and the cultivation reduced the SOC quantity in the greater than 20μm proportion greater than in the less than 20μm part signifying SOC accompanying with the less than 20μm is well conserved against degradation. On the other hand, soils having a high silt and clay amount may also allow the micro- and macroaggregates formation that can additionally protect the SOC, as soon as the microaggregates tend to be saturated with the organic matter, further the organic matter would mainly be present in the macro organic matter proportion, i.e., sand-sized (Carter 2000), then again cultivation may tend to breakdown this as seen by Hassink (1997). In the current literature in four soils from the United States have also stated that it is essential to make a distinction between various C proportions and the soil aggregates during the evaluation of C protection in the soils. The C proportion accompanying with the silt-sized finer particles (in the range of 2–20μm) was found to be not considerably controlled through tillage and the natural abundance of 13C measurements indicated it to be the oldest C proportion secluded from the macro- and microaggregates (Six et al. 2000a). The soil volume (that are stoniness and depth) and the bulk density are also essential when taking into account the SOC amounts on the areal basis, as is seen in the case of soil aeration (Batjes 1996). The mineralogy of clay and depth is basically constant and is not open toward the management. Whereas the stones could be eradicated from the sites (and also have been in some cases, so as to improve the tillage operations) and texture and bulk density can be altered by the application of sand (such as was made on a significant basis locally in the North Devon region, UK previous century), extensive alteration of either parameter is not practically feasible. This probable sequestration scenario is equivalent to the processes physiological in nature that estimate the potential in the crops.

The idea behind C stabilization in soil signifies that C stock in soil has reached the ultimate holding capacity for storage of C in soil (Six et al. 2002; Meena et al. 2020; Stewart et al. 2007). The onset is dependent on several factors that include dynamic and inherent soil properties as well as its interaction with non-biotic parameters, known as the maximum holding capacity of soil (Beare et al. 2014). This is indicative that when saturation level of C is reached, the process of SOC sequestration ceases and soils rather than becoming a C sink it may turn into the source of C. Microorganisms in soil play a critical role in CO_2 sequestration by altering the residues of plants into minor size C molecules which are ideal for protection and eventually sequestration (Six et al. 2006). Basically, the insects and worms found in soil transform the bigger residues of plants into small pieces that undergo metabolization by microorganisms like bacteria and fungi. During this entire process of degradation path, C molecules of varying sizes and different chemical compositions are released that are accompanied with clay and silt particles or get assimilated to form aggregates of soil (Six et al. 2006; Grandy and Wickings 2010). The fungi in the soil play a key role in SOC sequestration by improving the C distribution and also generates compounds which increases the stability of aggregate. For example, arbuscular mycorrhizal fungi (AMF) is a type of fungi that has a mutual association with the roots of plants. Consequently, AMF provides plants with nutrients to the soil whereas plants provide simple sugars to AMF (Govindarajulu et al. 2005). When plants feed upon the AMFs, the biomass tends to increase the C amount that is equivalent to the C amounts involved in the mechanism of photosynthesis in soil (Rillig et al. 2001). The AMF has an additional advantage of producing an extremely sticky protein known as golmalin which is useful in binding together soil aggregates that helps in protecting the soil C (Rillig 2004). The AMF has been found to have a positive correlation with C amounts and aggregation of soil (Wilson et al. 2009). Along with fungi, bacteria present in the soil have a key role in processing the organic matter found in the soil. The nitrogenous bacteria convert the complex compounds of nitrogen in organic matter into simpler forms easily available for uptake by plants. Conversely, actinomycetes play a key role in decomposing difficult form of C, i.e., lignin. These breakdown processes are responsible for enhancing the production of biomass and also ensure C gets converted to a stable form which remains safe in the soil (Six et al. 2006). Proper soil management practices for microorganisms in soil should be taken up such as wide inputs to plants, minimizing the tillage, etc., as these enhance the C sequestration capacity in soil (Six et al. 2006; Meena et al. 2020a). Even though soils have a huge capacity for C sequestration, there is a threshold for C saturation. At the point of C saturation, the soil will no longer act as a sink and may turn into a source of CO_2 or may also reach steady conditions during which C is attracted as much as it is emitted annually. Six et al. (2002) defined the saturation point of certain soil as the point where processes (such as adhering to mineral components, biochemical activity of protection, and aggregation) that protect soil C no longer protect the recent C.

The intrinsic soil properties, like type and clay content, hold a strong impact on such processes and hence strongly affect the saturation limit of soil. Likewise, previous studies reported that soils rich in smectite tend to protect greater organic

C compared to soils rich in kaolinite (Sorensen 1972; Ladd et al. 1992; Torn et al. 1997; Hassink 1997; Feller and Beare 1997; Wattel-Koekkoek et al. 2001). However, the soils globally are usually under saturation limit due to poor degradation and management (Lal 2004). Usually, saturation limit is defined as the ability of soil to behave as C sink tends to be limited. During the application of organic fertilizer along with clay matter, the C stabilization occurs effectively in soil. Bolan et al. (2012) suggested that the application of compost in soil containing higher amounts of clay materials tends to provide greater C stabilization. The advantageous characteristics of clay minerals such as physicochemical properties and crystalline structure in soil strongly impact the organic C stabilization. Wang et al. (2003) found that a sample of soil with twenty-three times more clay matter was able to minimize the respiration or C stabilization rate by around 50% in soil. Another previous study found that soil respiration reduced up to 40% with a twelve-time rise of clay content in soil (Franzluebbers 1999). It was reported that phyllosilicates of 2:1 type adsorb a higher amount of dissolved OC compared to clay minerals of 1:1 type. This is as a result of inherent physicochemical characteristics of specific minerals (Stotzky 1986; Singh et al. 2017a). For instance, smectite 2:1 type of clay minerals (like montmorillonite) comprises of greater specific surface area compared to clay minerals of 1:1 type (e.g., kaolinite). Montmorillonite has a specific surface area of 15–160 m^2/g, while the specific surface area of kaolinite ranges from 6 to 40 m^2/g. Montmorillonite has a smaller average particle size compared to kaolinite, that provides montmorillonite higher surface area in terms of per unit mass. Degree of replacing Al^{3+} in the octahedral sheet with $Fe^{2+/3+}/Mg^{2+}$ cations and Si^{4+} replacement in the tetrahedral sheet with Al^{3+}/Fe^{3+} cations is small for kaolinite, while significant in case of smectite. As a result, smectite has a greater layer charge compared to kaolinite, thus creating higher the active sites on the smectite surface. Higher the active site amounts on the surface of clay mineral would tend to greater adsorption of SOC theoretically. The CEC (cation exchange capacity) of kaolinite ranges from 0 to 100 cmol/kg, whereas smectite has a higher CEC value of 160 cmol/kg. Nevertheless, when subjected to certain experimental conditions, the pore size distribution and specific surface area of a clay mineral may get outdone by CEC of certain clay minerals in adsorption of organic C. On the other hand, when compared with smectite and kaolinite, the 2:1 mica type clay minerals (like illite) possess greater specific area in the range of 55–195 m^2/g with a moderate level of CEC (10–40 cmol/kg). On account of adsorption of organic C on the surface of clay minerals through different processes (such as electrostatic forces of attraction, ligand exchange, hydrophobic attraction), the organic C is protected from the attack of microorganisms (Singh et al. 2018; Baldock and Skjemstad 2000). In the present chapter, an attempt was made to review the role different clay minerals play in safeguarding the organic C present in soil and also discuss the processes involved in C stabilization by the clay minerals.

5 Properties Impacting Soil Carbon Sequestration

The dynamics of SOC present in the soil is affected by different factors such as soil type, surrounding climate, and management activities. These factors affect the presence of soil organic C, the biomass found in soil, and SOC loss through erosion and mineralization (Feller and Beare 1997). The factors are also influenced by the impact of biological, physical, and chemical materials on SOC. The dynamics of soil C is also responsible for the productivity and fertility of soil as well as functions of soil (Meena et al. 2018; Chen et al. 2004). There are other processes as well that affect SOC dynamics such as: (i) erosion causes removal in low-altitude sites with successive deposition, (ii) volatilization and degradation caused by movement of microbes, (iii) transport of OC particulates and DOC (dissolved organic C) with flow of water as seepage and runoff water, and lastly (iv) macro- and microaggregates stabilization affects the dynamics of SOC (Curtin et al. 2012).

The key source of SOC pool is the photosynthetically fixed C (Sanderman et al. 2010). The plants tend to transfer 20% (approx.) of C into roots by photosynthesis on an annual basis during the period of growth of vegetation (Whalen and Sampedro 2009). An estimate of 50% (approx.) of C is transferred under the ground in the agricultural lands is used up by the growth of roots (Johnson et al. 2006). Hence, the amount of C uptake on an annual basis by plants in a specific area estimates the C potential input in the soil (U.S. Department of Energy 2008). The presence of this C in soil acts as energy sources of flora-fauna in soil and their respective activities cause SOC degradation and their mineralization into CO_2 (Whalen and Sampedro 2009). The fauna in soil contributes significantly in C dynamics through disintegrating plant remains as well as various wastes from the farm and enables an appropriate surrounding for degradation of microorganisms. Nonetheless, macrofauna (in soil) such as earthworms is directly responsible for the degradation of OM in comparison to the microorganism in soil (Whalen and Sampedro 2009). The mechanism of soil respiration is the key way for the storage of CO_2 in soil via plants that are lost again back to the atmosphere (Follett 2001). The processes occurring on the soil surface such as erosion by running water/wind, leaching, and chemical oxidation lead to loss of SOC. The depletion of SOC is also caused by chemical oxidation, leaching, and erosion by wind or running water on the soil surface (Jong and Kachanoski 1988; Rhoton and Tyler 1990).

The difference in soil types, its suitability for several uses and soil formation factors must be taken into consideration by identification of management practices for advanced C sequestration. Organic C contents in peat soils that are drained artificially tend to increase unlikely, except when reverted to wetlands. This results in chances for higher C sequestration that are greatly limited to what is known as “upland soils”. Agriculture plays a role in sequestration of organic C content by soils which is unclear. Overall it is influenced by complicated factors such as economic, technological, cultural, and social. These factors should be addressed in particular in managing the sensitive and fragile ecosystems. Watson et al. (1996) stated 0.4–0.8 Pg C/year can be sequestered in the agricultural soils around the globe through the implementation of suitable management options. This further corresponds to about 10% of CO_2 globally through anthropogenic sources for the year 1990 (~6 Pg C/year).

Management options should be focused on CO_2-utilization optimally during photosynthesis to improve crop production and produces as well as also enhances specifically inactive or the mineral-stabilized section of SOC content pool. The available alternatives involve production of high residue, reduction in bare fallow, mulching, fertilization, and tillage options that are limited to depth and the disturbance intensities, particularly with phosphates (rock) and manure that are from the farmyard. The manipulation of the quantity and quality in organic inputs, such as the selection of cultivar and introducing the leguminous crops, and the soil fauna are options praiseworthy of further research (Torbert et al. 1997; Fernandes et al. 1997).

The extent to which different management practices would be effective is dependent on numerous environmental parameters, out of which some may be changed via climate change. As a result, management consequences of the enhanced CO_2 amounts and higher temperatures hence should be taken into consideration. The increase in atmospheric CO_2 amounts can stimulate the growth of crops until the nutrient supply or water can become limiting. This implies that the potential for extra application of fertilizer needs to be evaluated in terms of the soil type and crop (e.g., CAM or C3, C4 crops). Furthermore, land-users tend to only accept improved management practices if the profitability is improved within many years (Izac 1997).

The biofuels or energy crops hold a significant potential in mitigation of atmospheric CO_2 amounts by countering the utilization of fossil fuels. Production of biofuel in the range of 10–15% of land at present in agricultural usage or the agricultural settings can substitute for the 0.3–1.3 Pg C/year of the fossil fuel, on the other hand conversion and recovery of crop leftovers could replace for the extra 0.1–0.2 Pg C/year of the fossil fuel (Cole 1996). These numbers do not comprise of mitigating indirect atmospheric CO_2 through biofuel production by the increase in C storage in woody (standing) vegetation, and probably by higher C sequestration in soil. An only certain section of the leftovers of the biofuel crops could be detached without the adverse effect in soil productivity.

The forest management and reduction in tropical as well as subtropical deforestation could be feasible alternatives for the atmospheric CO_2 mitigation (Brown 1996). Such kind of initiatives would also minimize the ability of land degradation (specifically) anthropogenic, hence contributing toward the sustained production of food and security for the public in the area of concern.

The C sequestration in soil depends on balance existing between the input flow and output flow of C in the soil. This balance is positive in nature that exhibits C sequestration; on the other hand, negative C balance is associated with C degradation. The transport of biomass into soil and degradation of organic substances added are the two major processes that directly impact C sequestration in soil. The increase in production of biomass and additions in the soil tend to improve SOC to a certain point until it is dependent on tillage practices and various soil management activities. In accordance with cautious land use, the organic as well as inorganic C contents in soil can be enhanced (Meena et al. 2020b; Lal 2004). The soil characteristics,

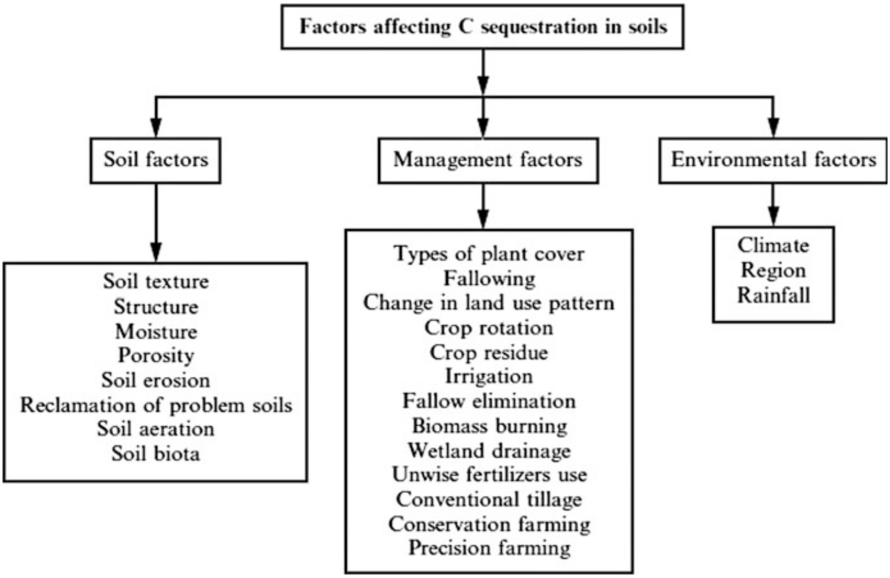

Fig. 2 Properties that affect carbon sequestration in the soil (Adopted, Lal 2003; Singh et al. 2017a)

management activities, and environmental settings are some of the factors, which impact C sequestration in the soil (Fig. 2).

5.1 Soil Characteristics

In the soil properties, the texture of soil plays a critical part in C sequestration. Hassink (1992) reported higher mineralization of C and nitrogen for soils with a coarser texture than that of soils with finer texture. These results tend to improve the ability of soils with a fine texture to protect OC physically from the attack of microbes (Hassink 1995). The texture of the soil is majorly responsible for C stabilization at shallow depths of land types such as lands for forest, crops, and shrubs (Fontaine et al. 2007; Albaladejo et al. 2013). In the case of soil dominant with clay, organic C has poor accessibility for the microbes in soil compared to sandy soil. This is because of the chemisorption of C on the clay mineral surfaces as well as occlusion (physically) inside the micro-aggregates (Sissoko and Kpomblekou-A 2010). Another key soil property is the structure of soil that shares a positive relationship with SOC. The minerals are held by SOC that forms soil aggregates and it contributes into SOC protection from degradation (Tisdall and Oades 1982; Elliott 1986; Gupta and Germida 1988). The soils with coarser texture (aggregates with lower stabilities) have a smaller capacity of C stabilization than that of aggregates found in the soil of fine texture, belonging to minimal tillage or natural ecosystems (Hassink 1992; Borchers and Perry 1992).

The moisture in soil significantly impacts the soil's ability to sequester C (Lamparter et al. 2009). The variation in moisture content tends to impact positively/negatively on the capacity of C sequestration in soils subjected to moderate/cold climates. As a result of this difference, degradation of plant remains and vegetation type could get affected (Sjogersten and Wookey 2009). In case of dry soils, the microbial activity is observed to be lower; while, higher SOC degradation is seen in wet soils, considering appropriate air circulation (Moyano et al. 2013). Nevertheless, the humid region soils have higher amounts of OC compared to dry region soils (Lal 2007). It is as a result of greater net primary production in humid region soils compared to dry region soils. The microbial activity of soil impacts the C dynamics in soil by emitting C as CO_2 back to the atmosphere via respiration. The microorganisms in soil play a key role in the respiration of soil and also contribute to the C mineralization of about 80%–95% (Hassink et al. 1994).

Some other pore structure (physical) characteristics of soils like dimension and number of pores majorly affect the presence and flow of water and air in the soil, that on the other hand influence the degradation of SOC (Baldock 2007). These pore structure properties influence the turnover of SOC; on the contrary, SOC amount and texture of soil in any particular soil also influence the porosity of the soil. The sandy soils offer little protection to SOC from the microbial attack as they possess higher amounts of large size pores and lesser amount of finer pores (Chivenge et al. 2007). The texture of soil, usually the amount of clay, plays a key role in protecting the loss of SOC from erosion (Sissoko and Kpomblekou-A 2010). The soil erosion comprises of aggregates breakdown, movement of particles of soil by air or water, and lastly, the eroded soil particles get redistributed (Lal 2004).

5.2 Management Activities

The management activities of land can significantly govern a soil's ability to act as a source/sink for C. Higher amounts of C input and minimized heterotrophic respiration aids in building the C amount in soils. With lesser cropping intensity as well as tillage in a controlled way can lower the rate of soil respiration, thereby improving C sequestration (Paustian et al. 2000). The variation in management activities from the conventional ways to zero tillage can improve the residence time of the SOC found in soil (Chivenge et al. 2007). Furthermore, the loss in stock of SOC during tillage is contributed by some properties that are (i) exposed-C mineralization after aggregates breakdown, (ii) dissolved C released by leaching, and lastly (iii) erosion through the movement of air or water (Rhoton and Tyler 1990). When tillage is not practiced, C stabilizes more in soil than that of conventional means of tillage as its forms aggregates that are stable in form (Devine et al. 2014; Follett 2001). The gain and loss of SOM is affected by management activities of land like frequency of cropping and system of cropping, minimized tillage, application of fertilizer/manure, and lastly cultivation of grasses and perennial legumes (Sommerfeldt et al. 1988; Campbell et al. 1991, 1995; Reicosky et al. 1995; Gregorich et al. 1996; Purakayastha et al. 2008a; Devine et al. 2014; Li et al. 2016; Cong et al. 2017;

Lopez-Bellido et al. 2017; Engel et al. 2017; Novelli et al. 2017; Yadav et al. 2017; Chaudhary et al. 2017; Conant et al. 2017). Among all these management activities, appropriate systems of cropping and optimal fertilization can contribute to highest potential for rise in SOC storage in the agricultural soils (Lal 2002a; Rudrappa et al. 2006; Collier et al. 2017; Shahid et al. 2017). The variation in management practices of agriculture tends to affect the OC dynamics of soil (Chivenge et al. 2007; Purakayastha et al. 2008b). Several agricultural practices related to management are responsible for SOC loss. These involve (i) ploughing, (ii) tillage in excess, (iii) deforestation, (iv) removal or burning of crop residues, and also (v) wetlands drainage (Lal 2002b). Management activities of agriculture addressing C sequestration involve incorporation of introduction of assimilated nutrient management, farming with precision, tillage conservation, rotation of crops, farm wastes usage, and setting up the plants on the contours and slopes (Chaudhary et al. 2017; Collier et al. 2017; Lal 2003). Moreover, it is well-known that on removal of naturally existing ecosystems tends to lower the SOC. The adverse impacts of agricultural management on the ability of soils for holding SOC can be described in two broader categories: (i) reduced inputs supply due to activities such as burning of stubble and due to outflow of C via harvesting the plant matter, and (ii) increased loss rate and reduced SOC level with cultivation (Skjemstad et al. 2004; Koga et al. 2016; Sun et al. 2016; Engel et al. 2017; Novelli et al. 2017).

5.3 Environmental Settings

The final balance (i.e., input-output) of SOC is also impacted by environmental properties such as moisture, temperature, as well as aeration. Rainfall and temperature are essential properties impacting C sequestration within soil as both factors contribute to production of biomass. Increase in temperature will raise the decomposition of SOC, on condition that an optimal level of moisture is present in soil (Singh et al. 2017b). The residual organic C gets stored in comparatively inactive C form that with slower turnover, nonetheless with a considerable amount of SOC would be respired when microbial activity increases (Canadell et al. 2007; Nishina et al. 2014). As a result of this, warm climates have soils that have lower SOC contents than that of soil in cold climates (Lal 2007). Rise in temperature has a negative relationship with SOC in soil, while with higher soil depth the temperature effect is less apparent as texture instead temperature contributes to C stabilization (Albaladejo et al. 2013). Humid region (such as tropical regions, boreal forests, wetlands, and savannas) soils are usually found to have a higher organic C content in dry region soils and it is because of higher biomass production found in regions with humid climate (Lal 2007). In case of dry soils, microbial activity is lower while SOC degradation is greater in the wet soils, on condition that good flow of air is prevalent. With the application of optimum amounts of moisture degradation and the SOC formation in soils could be improved (Wynn et al. 2006).

Historically, it has been seen that C content in soil decreases on cultivation, such reports were found for “virgin land system” for former USSR and “dust bowl” scheme of the United States and there were usually linked to lower levels of production, fertilizer application being inadequate, crop leftover removal, and also intensive tillage (Papendick 1994). Related examples of the continuous double multiplication of organic matter content in soils subjected to the century-long occupation of humans also persist, notwithstanding the smaller regions. Promising reports have recently become available based on improved C sequestration with grasslands in improved form and agro-ecosystems in both the temperate and sub-tropics areas, and also on the positive impacts on agro-forestry (Torbert et al. 1997; Fernandes et al. 1997; Batjes and Sombroek 1997; Paustian et al. 1997).

In case of tropical pastures, the root structure of plants could be used efficiently in sequestration and redistributing the C deeper within the profile of soil, where there are chances of better protection and less prone to degradation (Nepstad et al. 1991). The C sequestration in several grasslands within semi-arid regions could be raised through lowering in biomass burning, by improving the status of nutrients in the soil and also by bringing in legumes and improved grasses together with the measured stocking rates (Fisher et al. 1994).

With the enhanced land use, it has been estimated that decomposed (resilient) and cultivated soils depending on the management have the ability to sequester 0.1–1.0 Pg C/year (Lal et al. 1995). With an assumption since 1860 of C losses having 50–66% of the recovery, it was estimated that cultivated (improved) soils around the world can sequester 20–30 Pg C for the coming 50 years (Cole 1996). This result can be in the range of 23–44 Pg C if stable restoration and set-asides of decomposed lands can also be incorporated (Cole 1996). Globally, it has been reported that agro-ecosystems can be responsible for C sink, with the ability to absorb up to 7 Pg C for the coming 50 years with the utilization of suitable soil management activities (Sampson et al. 1993). This would result in an increase of production and also significant developments in management on most cultivated regions around the world, particularly in the less economically developed areas.

In the region of European Union, it is reported to have a certain potential to improve the soil C stocks over the coming decades by changing the agricultural practices, particularly in the perspective of the policies set-aside that are linked with the current overproduction in agriculture. Around 14 experiments were conducted for longer duration using regression analysis which showed that with the increase in the soil C over the coming 100 years through the application of manure from an animal, straw or the sewage sludge would account to be $<$ 15 Tg C/year (Smith et al. 1997a). This increase could be achieved in association with cropping on an annual basis, which implies a related removal of C present in agricultural produce. The higher potential would seem to occur by afforestation of excess arable land (~50 Tg C/year), and interchanging the present arable systems to ley/arable land (~40 Tg C/year) in that organic left-overs can be utilized again in the soil (Smith et al. 1997a).

However, in case of the new lands that are set-aside, the soil is not considered as a potential for enhanced C sequestration, when subjected to legumes or grass in combination with the application of phosphates (rock) and lime (Smith et al. 1997a). These kinds of scenarios hold value for future research for instance up to the range of 20–30% of cropland in the European Union would consist of land that is set-aside until the year of 2010. Conversely, if there is change in policies this alternative would not be available for longer, such as because of change in demands for fiber crops and food or recently apparent environmental urgencies.

There are also adverse side-effects to the environment during enhanced C sequestration that needs to be considered. Some of the measures which improve C sequestration in the soil and biomass, for example the addition of nitrogen fertilizers, tend to increase greenhouse gas emissions, for example, N_2O. In the rice wetland soils, application of freshly organic matter would lead to development and release of methane, which is a radiative active gas. The probable adverse side-effects to environment with extensive application of sludge and manure to the soil, by the increase in organic pollutant and heavy metal concentrations, must also be taken into account. The management and land-use practices that would minimize greenhouse gases emissions such as N_2O and methane have been studied extensively (Watson et al. 1996; Neue 1997; Smith et al. 1997b). These involve preserving the available forest cover, natural forests being regenerated, tree plantations being established, slow deforestation, agro-forestry promotions, transforming the management practices of rangelands and agricultural soils, improvement in the fertilizer use efficiency, restoration of degraded rangelands and agricultural lands, recovery of methane CH_4 from the stored manure, and improvement in the ruminants' diets quality.

6 Soil Organic Matter

The SOM is referred to as total amount of OC containing constituents present in soil. SOM is a section of soil that is composed of animal or plant tissue at various stages of degradation. The content of organic matter in various types of soil generally ranging from $<1\%$ (in desert type of soils) to around 100% in the organic-rich soils. The SOM has greater OC than atmosphere and global vegetation combined together. Due to this emission and transformation into CO_2 or CH_4 of even slightest fraction of C present in SOM can lead to significant variations in atmospheric amounts of such greenhouse gases. Furthermore, the organic matter available in the soil holds the nutrients along with pollutants that improve growth of the plants and protect water quality. Soil essentially contributes to source of C in aquatic environment with effects in biogeochemical processes in lakes, river, and estuaries. In spite of the identified importance of SOM, its nature is viewed variedly. The physical, biological, and chemical conversion processes that transform dead plant residues to organic substances which form close links with minerals found in soil that arises complexity in understanding the nature of SOM. Stevenson (1982) states that the soil organic matter greatly affects plant growth with effect on physical, biological, and chemical characteristics of soil. It improves the soil structure that promotes aeration, tilth, and moisture flow plus retention. It has capability to react with clay minerals, metal oxides, metals, and hydroxides that form complexes of metal-organic type and plays the role of ion exchanger and store as nitrogen, sulfur, and phosphorous. SOM also provides C as a source of energy to nitrogen-fixing bacteria, yield, root initiation, growth of plant, chlorophyll synthesis, nutrient uptake, and germination of seed (Prakash and MacGregor 1983). SOM is basically composed of 10% carbohydrates; 10% of nitrogen constituents (which include protein, amino acid, peptides, pyrimidines, purines, amino sugars, and some unidentified compounds); 15% of fatty acids, alkanes, resins, waxes, etc., and rest 65% of humic materials.

There exists a great difference in the quantity and the organic matter vertically distributed in the boreal, tropical, temperate, and also subtropical soils. The SOM that is stored in the top of soil is responsible for nutrient cycling occurring in soil-plant-water structure and gaseous exchanges in the atmosphere (Nepstad et al. 1991; Davidson et al. 1993).

The organic matter in soil can be categorized into three types, which are: the microbial biomass, i.e., living as well as plant residues, the detritus made of active SOM and lastly humus made up of stable SOM. The microbial biomass, i.e., living involves microorganisms that degrade both detritus and plant residues. Humus is formed due to decomposition of animal and plant tissues and is the final produce of degradation. The microbial biomass (living) plus plant residues and detritus types of OM add to the soil fertility due to degradation of these sections resulting in release of nutrients of plants like potassium, nitrogen, phosphorous, etc. Humus does not improve the fertility of soil but improves the aggregate stability, enhancing water infiltration plus soil aeration and minimizing the runoff. The humus helps in improving the water holding capacity, cation exchange capacity of the soil and capability of the soil to prevent change in pH. The humus also improves pore space due to the movement of microorganisms in soil, enhances infiltration, and minimizes runoff. Schnitzer and Khan (1975) divided SOM into the humic and the non-humic substances. The non-humic materials include substances with chemical properties such as proteins, amino acids, carbohydrates, peptides, waxes, resins, fatty acids, etc. These types of compounds get easily decomposed in soils and life span is shorter. Nevertheless, humic materials comprise the bulk of the soil organic matter. The humic substances are dark in color, amorphous in nature, majorly aromatic, partially aromatic, and complex chemically with molecular weight ranging from few hundred-many thousand (Schnitzer and Khan 1975).

With increase in levels of soil organic matter, the crop yield and productivity of soil is benefited (Greenland 1997; Goh 2001; Edmeades 2003). These are aligned with benefits associated with higher amounts of soil C sequestration in climate change mitigation. At any point of time, the organic C present in soil is dependent on complex reactions existing between climate and biological, physical, and chemical processes occurring in soil (Fenton et al. 1999; Goh 2001).

7 Soil Organic Carbon Stabilization

The process of OC stabilization in soil is an act that reduces the degradation of SOC by lowering mineralization rate. The SOC stabilization undergoes three mechanisms in soil that are: (i) physical, (ii) chemical, and (iii) biological which are discussed in this section below (Stevenson 1994, Christensen 1996). The mechanism of chemical stabilization of SOM is assumed to be as a result of the physicochemical or chemical binding occurring between the soil minerals and SOM (i.e., silt and clay particles). Numerous previous studies have been reported that exhibit a correlation existing in between organic C and nitrogen stabilization in the soils and the clay/silt as well as clay content (Sorensen 1972; Merckx et al. 1985; Ladd et al. 1985; Feller and Beare 1997; Hassink 1997). In addition to the clay content, clay type (i.e., 2:1 versus 1:1 versus allophanic clay minerals) influences the stabilization of organic C and N (Feller and Beare 1997; Ladd et al. 1992; Sorensen 1972; Torn et al. 1997). Physical protection by aggregates is indicated by the positive influence of aggregation on the accumulation of SOM (Edwards and Bremner 1967; Elliott 1986; Jastrow 1996; Tisdall and Oades 1982; Six et al. 2000b). The aggregates tend to protect SOM physically as a result of formation of obstacles physically in between enzymes and microbes as well as their substrates and governing food web relations and subsequently microbial turnover (Elliott and Coleman 1988). The biochemical stabilization process is known to be the SOM stabilization because of the chemical composition of its own (such as recalcitrant compounds, e.g., polyphenols and lignin) and by processes of chemical complexing (like condensation reactions) in the soil.

7.1 Physical Stabilization

This type of OM stabilization is because of protection from physical obstructions formed in between the zone of degradation of organisms and the SOM (Elliott and Coleman 1988). This position of OM and input flows in the various levels of soil are critical in controlling the movement of the organic matter toward microorganisms. The segregation of soil microorganisms and the substrates through micro- and macroaggregates is clearly visible by the amount of the microbes being highest in the outside periphery of aggregates (Hattori 1988). Although considerable amount of SOM is observed at the middle of the aggregates (Golchin et al. 1994; Tan et al. 2017). Several reports have shown positive correlation between aggregation and soil OM accumulation (Six et al. 2000c, Paustian et al. 2000; Pulleman and Marinissen 2004; Yu et al. 2015). With cultivation, C is released due to the breakdown of aggregate structures in soil which increases the presence of C degradation (Zhang et al. 2017). Basically, cultivation causes the conversion in macroaggregates that are C rich into microaggregates that have lost C and also textural fractions (Six et al. 2000b; Lopez-Bellido et al. 2017). Nonetheless, the SOC is usually safeguarded from decomposition during sealing of microaggregates and these microaggregates are found in macroaggregates that are greater than 250μm (Besnard et al. 1996; Skjemstad et al. 1996; Six et al. 2000c; Yang et al. 2017a).

7.2 Chemical Stabilization

The SOM is stabilized because of the physicochemical or chemical binding to the surfaces of minerals in soil based on assumptions. This type of complexes that are organic-mineral in nature are pivotal to soil C cycle as this tries to stabilize the SOC from the microbial attack. The adsorption of DOC in subsoil causes decrease in mineralization by around 30% than compared to mineralization taking place in soil solution (Kalbitz et al. 2005). The SOC has stability, i.e., highly effected by amorphous nature as well as poor crystalline structure of mineral constituents with higher OH groups (or greater chemical capacity) and that helps in establishing relationship with organic matter in terms of OC, i.e., mineral safeguarded (Mikutta et al. 2005; von Lutzow et al. 2007; Kleber et al. 2007). These kinds of organic-mineral relationships are due to the greater molecular interactions existing in between OH group of Al and Fe-oxyhydroxides and also the hydrophobic functional group present in OM (von Lutzow et al. 2006; Kleber et al. 2007). The iron and aluminum oxides and clay minerals play a critical role in the adsorption of dissolved organic C (Bolan et al. 2011; Singh et al. 2016, 2017b). In particular, iron oxides contribute significantly to adsorption and the SOC stabilization (Kaiser and Guggenberger 2003). The phyllosilicates are also responsible maintaining DOC (Feng et al. 2005). Dissolved organic C adsorption on the clay mineral surface is based on the selectivity toward hydrophobic and aromatic compounds (Kaiser and Guggenberger 2000). This stabilization of OC in the soil is controlled by adsorption of DOC on the silicate mineral layers. However, it was also found that the influence of links between the hydrous Fe oxides and the clay minerals with silicate layer on adsorption of DOC is unpredictable (Saidy et al. 2012, 2013).

7.3 Biological Stabilization

The complexity in chemical structure of OM is responsible for stabilization of OC in soil or biological protection. The mechanism of stabilization occurs by their intrinsic biological resistance to degradation. The physicochemical interactions between clay minerals are also a mechanism involving SOC stabilization. Organic molecules that are polymeric in nature also containing aromatic rings are highly resilient to decomposition. These are namely, lignin and also various types of the polymethylenic molecules (like lipids, wax, cutin) (Derenne and Largeau 2001). In initial stage of decomposition of plant residues, these constituents are conserved (Kalbitz et al. 2003a, b). On the other hand, recent study found that long-range lignin compounds get stabilized in larger fractions in soil and have no contribution toward refractory components in SOC (Rumpel et al. 2002; von Lutzow et al. 2006). This gets converted faster compared to few different constituents of SOC like polysaccharides which have microbial origin (Kiem and Kogel-Knabner 2003; von Lutzow et al. 2006). Lignin is identified to be recalcitrant by complex structure and available of non-hydrolyzable bonds. In comparison to protein and cellulose, this type of aromatic molecule undergoes slow degradation by the action of enzymes (Haider 1992; Kirk 1984; Martin et al. 1980).

8 Interaction of Clay Mineral with Organic Matter

There are assumptions that most of humic components in soil are firmly attached to the minerals surfaces which are colloidal in nature and is found in clay and silt that is attached to OM older in origin having higher turnover time (Scharpenseel and Beckerheidmann 1989; Balesdent 1996; Quideau et al. 2001; Ludwig et al. 2003; Eusterhues et al. 2003). The clay minerals found in the soil sorb various kinds of organic compounds by various mechanisms, namely, (i) electrostatic forces of attraction, (ii) ligand exchange, (iii) cation (polyvalent) bridging, and (iv) van der Waals forces and hydrogen bonds (Oades 1989; Vermeer et al. 1998; Vermeer and Koopal 1998).

8.1 Electrostatic Forces of Attraction

Organic molecules have been known to be held in the clay surfaces by coulombic forces and van der Waals forces of attraction (Hendricks 1941; Grim et al. 1947; Talibudeen 1950). The electrostatic attraction existing in organic substances and mineral surfaces in soil can happen by cation exchange. This type of reaction takes place once positive charged organic substances substitute inorganic cations (Wang and Lee 1993). Density of "+" charge is weak for fundamental organic molecules and also dependent on pH strongly. Thus, adsorption during these kinds of interaction is affected by combined organic substances and the soil pH. Moreover, length of the chain of organic molecules as well as type of the cations on exchange sites controls the bonding strength. These kinds of interchange happen on the phyllosilicates (expandable 2:1) interlayer surfaces resulting in entry of organic substances within the interlayer spaces, and this process is known as intercalation (Sarkar et al. 2013; Lagaly et al. 2013). Intercalation degree influenced by shape and size of the organic substances as well as by density of charge in mineral surfaces. Even though intercalation can sometimes be considered as potential mechanism of SOM stabilization and also in field finding to support when limited (Leinweber and Schulten 1995; von Lutzow et al. 2006; Skiba et al. 2011). However, Theng et al. (1986) established the presence of microbial activity in soil during cold climate and thus resulting in minimal degradation of intercalated organic matter.

8.2 Ligand Exchange

The strong associations between organic and mineral components occur by development of the covalent bonds existing in between OH groups on mineral surfaces and phenolic hydroxyl groups and carboxyl groups of organic substances. The reaction of ligand exchange is found to be useful in OM stabilization from the microbial degradation (Mikutta et al. 2007). The correlation of OM and mineral surfaces through ligand exchange rises as pH decreases and ultimate complexation happens in the pH range of 4.3–4.7 that corresponds to values of pK_a of prevailing carboxylic acids present in soils (Gu et al. 1994). The soils that are acidic in nature, with hydroxyl groups of Al, Mn, and Fe oxides and cracked sides of phyllosilicates can have positive charge and also interact with phenolic OH and organic carboxyl groups. Therefore, these kinds of reactions are limited to the acidic soils that are abundant in the mineral surfaces along with the protonated OH group (Shen 1999).

8.3 Cations (Polyvalent-Type) Bridging

The mineral surfaces with negative charge tend to repel anions (organic molecules); however, the occurrence of cations (polyvalent ones) on exchange complex benefits binding existing in between. In case of alkaline and neutral soils, Mg^{2+} and $Ca^{2+}$are dominant cations, while of Al3+ and Fe3+ (hydroxyl-poly-cations) are majorly present in acidic soils. These kinds of ions with positive charge get adsorbed on mineral surfaces having negative charge and assists in adsorption of long-chain organic components with negative charge via the mechanism of bridging the cation (Sposito et al. 1999; von Lutzow et al. 2006; Yang et al. 2017b). The Ca^{2+} ions unlike Al^{3+} and Fe^{3+} ions do not exhibit the formation of coordination complexes that are strong enough along with the organic ions. The organic molecules with long-chain take along several sites that are negatively charged because of the occurrence of uronic acids which strongly adsorb on numerous sites of layer silicates having permanent charge which are expandable type via cation bridging (polyvalent). The OM cation bridging through carboxylic group, to negative charge (permanent) clay surfaces denotes an essential method of binding for accomplishing SOC stabilization within several soils (Arnarson and Keil 2000; Mikutta et al. 2007; Yang et al. 2016). Moreover, the role of organic anions (polar) that form bonds with water bridging in metals is an essential OM adsorption process (Sutton and Sposito 2006). The OM binding by the action of cation bridging is weak compared to ligand exchange attained via adsorption (Benke et al. 1999; Kaiser and Zech 2000). Overall, adsorption of OC on clay mineral surfaces follows the following order: hydroxides/oxides >clay minerals of 2:1 type> clay minerals (1:1), and this behavior is influenced by CEC and the SSA of particular minerals.

8.4 van der Waals Forces and Hydrogen Bonding

Hydrogen bonding and van der Waals forces, along with hydrophobic forces, are some of the other interaction mechanisms contributing to organic substances complexation the surface of minerals. The van der Waals forces act in between entirely the molecules and from the variations in the density of particular atoms of electric charge. Basically, these kinds of forces occur in between the atoms or the nonpolar molecules because of the temporarily varying dipole moment of 1 molecule that releases a dipole toward neighbor; it is known as an induced dipole bonding. The role of van der Waals forces to binding mechanism is majorly influenced by the surface area (contact) and polarizability of organic substances. In hydrogen bonds, hydrogen atom, i.e., partially "+" charged interacts with a neighboring, partially "−" charged O or N atom. The extracellular enzymes and polysaccharides or various other protein molecules create associations through hydrogen bonds or van der Waals forces because of the availability of OH and various type polar groups in molecules (Quiquampoix et al. 1995).

9 Interaction Between Clay Minerals and Organic Matter in the Soil with Relevance to Carbon Stabilization

In the longest time, a concept is popularly known that the clay components present in soil contribute significantly in stabilization of soil organic C (Jenkinson and Rayners 1977; Tisdall and Oades 1982). Previous studies have shown that C is highly enriched in clay fractions in comparison to silt and sand particles and also irrespective of soil depth and type (Rumpel et al. 2004). The clay minerals along with OC act as framework for the formation of microaggregates (Tisdall and Oades 1982).

9.1 Soil Organic Carbon Stabilization and Phyllosilicates

The effect of phyllosilicate minerals on SOC stabilization has been determined by organic matter decomposition and investigations are carried out for longest period in vitro settings (Jones and Edwards 1998; Chevallier et al. 2003). Several mechanisms occur that contribute to reduction in decomposition rate: (i) extracellular enzyme that decomposes OM is found to be inactive during adsorption on clay minerals, (ii) substrate organic substances that are adsorbed on clay is absent for microbial enzymes (extracellular ones), (iii) pH is buffered by phyllosilicates, (iv) other important compounds adsorbed on clay minerals plus considered unreachable to the microorganisms, and (v) the phyllosilicates directly impact on either raising or lowering the microorganisms activity (Chenu and Stotzky 2002). Numerous literature stated highlight absence of decomposition of organic substrates that are adsorbed (Smith et al. 1992; Lozzi et al. 2001; Chevallier et al. 2003; Chen et al. 2009; Besse-Hoggan et al. 2009). O'Loughlin et al. (2000) stated that reduction in decomposition rate corresponds to rise in binding capacity that is in the following order: montmorillonite>hectorite>illite>kaolinite. Several reports found that interaction strength considerably influences OM decomposition rate (Chen et al. 2009; Cai et al. 2011). Some literature reported the role of various pure minerals that were applied to the soils helped in protecting OC (Sørensen 1972; Saidy et al. 2012). Literature compares associated SOC amount with clay minerals or the turnover rate of SOC in C fractions that are mineral-associated in soils that have dissimilar phyllosilicate mineralogy (Amato and Ladd 1992; Saggar et al. 1996; Wattel-Koekkoek et al. 2003). However, the C mean residence time was higher on an average aimed at C-associated smectite. Conversely, one study found that the kaolinite- and smectite-associated C portions had similar mean residence time that were taken from 10 types of soils from Mozambique (Wattel-Koekkoek and Buurman 2004). These contradictory findings were explained by the CEC of the clay fraction which play a key role in stabilization of C in soil to higher level compared to clay mineralogy. The soil mineralogy plays important role in determination of organic C amount that are stored in the soils plus their turnover time (Torn et al. 1997). Generally, it has been assumed that sequestration of SOM using minerals lowers in following sequence: allophane>smectite>illite>kaolinite (von Lutzow et al. 2006; Bruun et al. 2010). Nevertheless, this behavior varies depending on the soil having Al and Fe oxide amounts (Singh et al. 2017b). Organic cations easily replace inorganic cations that are adsorbed electrostatically on phyllosilicates external surface. This kind of reaction can also happen on the interlayer surfaces with layer silicates (expandable 2:1), that have organic compounds entering the interlayer areas (Sarkar et al. 2011, 2012, 2013; Lagaly et al. 2013).

9.2 SOC Stabilization and Secondary Minerals

The SOC stabilization (chemically) is relative to the presence of mineral surfaces that can adsorb SOC and also availability of functional groups (reactive) on surface of minerals. In case of metal oxides, aluminum and iron oxides are identified as main sorbents for the formation of organic and mineral interactions in the soil (Huang 2004). Some studies using FTIR spectroscopy found that the surface OH groups of the metal oxides contribute significantly to the retention of organic substances. These kinds of functional groups go through rapid reaction such as: ligand exchange with the carboxyl group or/and hydroxamate groups in organic substances that form metal-O-C bonds (polar covalent in nature) (Borer et al. 2009; Chernyshova et al. 2011; Borer and Hug 2014; Greiner et al. 2014). Phospholipids have phosphoester groups in the extracellular substances (polymeric type) in microbes are also involved in reactions between ligand exchange and metal oxides (Omoike et al. 2004; Omoike and Chorover 2004; Cagnasso et al. 2010). The OC stabilization in soil rich in iron and aluminum oxides is controlled by (i) OM protection by Al, Fe, and allophane complexation, (ii) minimize the bacterial activity resulting from presence of free Al and Fe, and (iii) lower pH values and less amounts of nutrients, specifically P to the microorganisms present in soil that take part in SOC decomposition (Parfitt 2009; Bolan et al. 2012).

9.3 Soil Carbon Sequestration and Weathering of Rocks

During weathering of the silicate minerals like basalt, base cations like (Mg^{2+}, Ca^{2+}) are released that consequently nullifies by carbonic acid reactions and CO_2

sequestration occurs in the carbonate/bicarbonate minerals that gets deposited on ocean floor (Kohler et al. 2010; Hartmann et al. 2013; Taylor et al. 2016). Previous studies stated that weathering of minerals in rock could be improved with various physical and biological processes with application to soil simultaneously that benefits production of crops and climate globally (Quirk et al. 2014; Taylor et al. 2016; Edwards et al. 2017; Kantola et al. 2017). The cations that are released after basalt/olivine dissolution can precipitate in soils forming carbonate minerals when supersaturation happens chemically (Manning and Renforth 2013; Renforth et al. 2015). Furthermore, these cationic species accumulate on spent mineral surfaces and SOC is attracted via reactions of cation bridging. The cations tend to increase the soil CEC and the base saturation together helps in improving SOC sequestration (Gillman 1980; Gillman et al. 2001).

Likewise, rock minerals of colloidal-sized fraction also have tendency to directly sorb DOC and are prevented from microbial degradation. As a result of existing chemical conditions in soil, the elements released also tend to re-precipitate thereby forming new mineral minerals that are poor- or non-crystalline. These kinds of new minerals can also take part in SOC sequestration via mechanisms of electrostatic attraction and ligand exchange (Yu et al. 2017). Eventually with time, rock minerals would form clay minerals helping in increasing the OC retention and enhancing CEC in soils.

10 Conclusions

In the recent times, new concerns have arisen regarding the ability of soil to store C for long periods as well as mechanisms that can quantify C storage. SOC dynamic modeling has been identified to be an invaluable technique involved in predicting climate change influence on CO_2 storage as well as also assists in developing advanced approaches to reduce GHG emissions. The requirement of scientific data in modeling is a major challenge. However, the advancement in technology and soil management practices can help in sequestering greater amounts of CO_2 in soil.

Moreover, addressing the relationship between C stabilization and clay minerals would lead to the development of efficient climate change policies and soil management practices. The different properties of clay minerals (that contribute to feedback mechanism for SOC stabilization) available in the soil greatly control the physicochemical factors of a soil. Usually type and amount of clay minerals available in a soil remains unchanged, understanding processes involved in clay-controlled SOC stabilization is essential for CO_2 sequestration in the longer periods. Nevertheless, only some extensive studies are available on associations of clay minerals plus soil organic C stabilization. The influence of climatic conditions on mineralization arrangement of clay minerals-holding SOM is limited and needs to be thoroughly investigated. Likewise, the influence of introduction of recent OM in clay containing soils rate of C mineralization needs to be understood. In addition to these concerns, efforts are needed to develop techniques to determine various SOC pools and pathways to help in making soil modeling (specifically GHG emission) more practical.

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Microbial Potential for Carbon Fixation and Stabilization

Meenakshi Sharma, Rahul Datta, Vivek Kumar Kedia, and Martin Brtnicky

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Abstract

Research on microbial diversity, interaction between microbes and soil physiochemical properties, role of microbes in biogeochemical cycles, and climate change have guided the scientific community to understand the soil and environmental health. Carbon is one of the essential elements of the soil, oceans, atmosphere, crustal rocks, kerogen (solid hydrocarbon for the formation of fuels), and reserve in various forms called carbon sink. Carbon-containing organic molecules flux between all these ecosystems (reservoirs) for the balance and sustainable function of the ecosystems via active carbon cycle. Carbon is the prime element for building a life on Earth which is fixed in various forms in the terrestrial and marine plants through photosynthesis. Microorganisms play regulatory role in biogeochemical cycles and shaping any kind of ecosystems. There are huge diversity of soil and aquatic microbes like *Acetobacterium woodii, Aquifex aeolicus*, *Archaebacteria brierleyi*, *Ignicoccus hospitalis*, *Chlorobium limicola*, *C. tepidum*, *C. thiosulfatophilum*, *C. phaeobacteroides*, *Chloroflexus aurantiacus*, *C. aggregans*, *Chromatium vinosum*, *Clostridium thermoaceticum*, Crenarchaeota, *Desulfobacter hydrogenophilus*, *Desulfurobacterium crinifex*, *D. thermolithotrophum*, *Halobacterium salinarum*, *Thiobacillus ferrooxidans*, *Hydrogenobacter hydrogenophilus*, *H. thermophilus*, *Metallosphaera sedula*, *Moorella thermoacetica*, *Pyrobaculum aerophilum*, *Pyrobaculum islandicum*, *Pyrolobus fumarii*, *Rhodobacter sphaeroides*, *Rhodopseudomonas viridis*, *Rhodospirillum rubrum*, *Stygiolobusa zoricus*, *Sulfolobus metallicus*, *Sulfurihydrogenibium subterraneum*, *Thermocrinis ruber*, *Thermoproteus neutrophilus*, *Thermovibrio ammonificans*, *T. ruber*, and *Thiomicrospira denitrificans*, and also order Rhizobiales are able to fix the various forms of carbon through numerous pathways such as Calvin cycle, reductive acetyl-coenzyme A pathway, reductive citric acid cycle, dicarboxylate/4-hydroxybutyrate cycle (DC/HB), hydroxypropionate/4-hydroxybutyrate cycle (HP/HB), and 3-hydroxypropionate bicycle. The fixed carbon is used by these microbes for their growth and development and also to make it available for other organisms. The carbon sequestration efficiency of plants and microbes by biotic (photosynthesis and respiration) processes plays key crucial role in mitigation of global climate change and environmental stability. In spite of the use of modern biotechnologies in research, huge information of microbial diversity and role in balancing of biogeochemical cycle are still not fully known. Therefore, it is crucial to discuss in-depth the scientific knowledge of microbial carbon fixation processes and its role in the mitigation of global climate change in present era.

Keywords

Acetogens · Biogeochemical cycle · Calvin–Benson–Bassham Cycle · Carbon cycle · CO_2 fixation · Crassulacean Acid Metabolism or CAM Pathway · Hatch and Slack Pathway or Dicarboxylic Acid Pathway or C4 Cycle · Global climate change · Methanogens · Reductive Acetyl-Coenzyme A Pathway or Wood–Ljungdahl pathway · Reductive citric acid cycle · Dicarboxylate/4-hydroxybutyrate cycle (DC/HB) · Hydroxypropionate/4-hydroxybutyrate cycle (HP/HB) · 3-Hydroxypropionate bicycle

Abbreviations

3HP/4HB	3-Hydroxypropionate/4-hydroxybutyrate cycle
AACT	Acetoacetyl-CoA β-ketothiolase
ACC	Acetyl-CoA/propionyl-CoA Carboxylase
ACC	Acetyl-CoA/propionyl-CoA carboxylase
ACR	Acryloyl-CoA reductase
ACS	Acetyl-CoA Synthase
bR	Bacteriorhodopsin
CAM	Crassulacean acid metabolism
CCH/HBCD	Bifunctional crotonyl-CoA hydratase/(S)-3-hydroxybutyryl-CoA dehydrogenase
CCL	Citryl-CoA lyase
CFe-SP	Corrinoid iron-sulfur protein
CODH	Carbon monoxide dehydrogenase
CUE	Carbon use efficiency
DC/HB	Dicarboxylate/4-hydroxybutyrate cycle
FD	Ferredoxin
FDH	Formate dehydrogenase
GPB	Green phototrophic bacteria
H_4F	Tetrahydrofolate
H_4MTP	Tetrahydromethanopterin
HBCD	4-Hydroxybutyryl-CoA dehydratase
HBCS	4-Hydroxybutyryl-CoA synthetase
HP/HB	Hydroxypropionate/4-hydroxybutyrate
HPCD	3-Hydroxypropionyl-CoA dehydratase

HPCS	3-Hydroxypropionyl-CoA synthetase
MCE	Methylmalonyl-CoA epimerase
MCM	Methylmalonyl-CoA mutase
MCR	Malonyl-CoA/succinyl-CoA reductase
MSR	Malonic semialdehyde reductase
OAA	Oxaloacetic acid
OSR	Oxalosuccinate reductase
PCR	Photosynthetic carbon reduction
PEP	Phosphoenolpyruvate
PNSB	Purple non-sulfur bacteria
RPP	Reductive pentose phosphate
rTCA	Reductive tricarboxylic acid
RuBisCO	Ribulose-1,5-bisphosphate carboxylase/oxygenase
RuBP	Ribulose-1,5-bisphosphate
SLP	Substrate level phosphorylation
SSADH	Succinic semialdehyde dehydrogenase
SSR	Succinic semialdehyde reductase

1 Introduction

Biogeochemical cycles are the fundamental part of any ecosystem on Earth, which is critically controlled by transforming elements into molecules and flux from one reservoir to another with the balanced rate (Nazaries et al. 2013; Tomkins and Müller 2019). Next to water, carbon is one of the essential elements of any ecosystem and backbone of all living organisms to survive on Earth, constituting approximately 45–50% of all dry biomass (Thauer 2007b). Soil is the biggest terrestrial ecosystem for carbon reservoirs approximately 1500–2500 Pg, whereas the atmospheric carbon reservoirs are 590–760 Pg and terrestrial vegetation 350–550 Pg C. The total Earth carbon sink contains approximately 43×10^{18} g (Whitman et al. 1998; Lal 2004; Batjes 2014; Meena et al. 2020b; Smith et al. 2015). Carbon cycle is one of the most crucial biogeochemical cycle where carbon atoms flux from the atmosphere to the Earth and then return to the atmosphere (Fuchs 2010). Carbon dioxide (CO_2), the most abundant and crucial inorganic form of carbon present in the atmosphere, serves as a prime source of carbon for the plants and other microorganisms. The major sinks of carbon content on our planet are (1) terrestrial biosphere where carbon is present as organic molecules in living and dead organisms; (2) atmosphere where carbon is present in gaseous form (CO_2); (3) lithospheric carbon, in the form of fossil fuels and sedimentary rock; and (4) oceanic carbon present abundantly as dissolved atmospheric carbon dioxide and calcium carbonate ($CaCO_3$) (York 2018; Tomkins and Müller 2019).

The carbon cycle is completed by various steps: 1. Carbon starts its cycle when it is absorbed by the producers and assimilated through photosynthesis into glucose. Animals consume the plants and give way to carbon to enter the food chain. 2. Once the plant and animal die, decomposers break down the dead organisms and return the

CO_2 to the atmosphere. Some of the carbon of dead organisms remain blocked and form fossil fuel which is used in the combustion process. The carbon cycle needs to maintain the balance between both the process of photosynthesis and decomposition (Fernández-Martínez et al. 2014). The Earth represents the closed system, so the amount of carbon on the planet remains constant. However, it is present in various organic and inorganic forms which can be stored for several years and can be exchanged between various carbon reservoirs in few seconds to millions of years. For example, some carbon in the atmosphere might be captured by plants to manufacture food during photosynthesis. This available carbon can then be utilized by the animals that eat the plants and stored for a certain period. Decomposed parts of dead animals and plant tissues with their remains become sediments and construct the carbon layers. Under different circumstances, sediments turn into minerals and fossil fuels such as coal, oil, or natural gas. Most of these fossils fuel components burn and release carbon back into the atmosphere. In present era, global climate change crisis is the major issue and which can be solved by reducing the CO_2 emission on urgent basis and increasing the biological CO_2 fixation. The atmospheric CO_2 fixation is not only carried out by the plant, but soil and oceanic microorganisms also play a crucial role in the global carbon cycle (York 2018; Tomkins and Müller 2019; Dang 2020).

Microbes like cyanobacteria, protobacteria, green sulfur and non-sulfur bacteria, microaerophiles, methanogens, acetogens are extensively studied and reported to fix huge amounts of CO_2 in different carbon reservoirs (Thauer 2007b). Most of the autotrophs majorly fix the atmospheric CO_2 via Calvin cycle. Still, various other alternative complex pathways such as reductive acetyl-coenzyme A pathway, reductive citric acid cycle, dicarboxylate/4-hydroxybutyrate cycle (DC/HB), hydroxypropionate/4-hydroxybutyrate cycle (HP/HB), and 3-hydroxypropionate bicycle are also reported in some unique microbes. Based on modern molecular techniques like metagenomics, soils are huge self-organized ecosystem where complex diversity of microbes are present. A little information is available about the soil microbial diversity, most of which is still uncharacterized. The metagenomics research tells us that any sample consists of great amount of microbial diversity (>99%) which is yet to be discovered (Jurasinski and Koch 2011; Meena et al. 2020a; Delmont et al. 2011). Most of the active biogeochemical cycle greatly controlled and shaped by the microbial community and the major amount of carbon flux between different carbon sink are crucial to maintain atmospheric climate. Therefore, it is necessary to understand the huge microbial diversity and their crucial role in regulating carbon concentration in various biogeochemical cycles (Gilbert and Neufeld 2014).

2 Soil Microbial Diversity

The earliest life form on our planet is microbes based on their presence in rocks about 3.7-billion-year-old, while animals and plants have reported only about 3000 millions of years (Bell et al. 2015). Dutchman Antonie van Leeuwenhoek observed the microorganisms under the simple microscope in 1675. In the nineteenth century, many scientists explored the microbial world drastically. Microorganisms are very small forms and present everywhere on the Earth as single cells, also form colonies of cells, and play a key role in balancing all life forms. Microorganisms and their physio-biochemical processes are very crucial for earth functioning. Various extensive studies on metagenomic analysis, represents that soil microbial diversity is extremely complex and majorly undiscovered. The complex microbial diversity and their different biochemical pathways play critical role in environmental health management (Sharma and Gautam 2018). Microorganisms not only provide innovative applications to the soil, water, and air but also are very crucial for the life of plant and human. Nutrient cycling, biodegradation and decomposition, climate change, food processes, and several other mechanisms are very much controlled by the microbes (Gilbert and Neufeld 2014). A variety of microbes exist throughout the Earth and have a fundamental role for the health of the soil, water, and air. The richest inventory of living creature on Earth is microbes. Approximately, 60% of the total biomass of the Earth constituted by the microorganisms. One gram of soil consists of millions to billions of microbes. The recent information suggests that our Earth consists of more than 5–6 × 10^{30} prokaryotic cells, the soil represents around 4.5 × 10^{30}, and ocean represents 3.6 × 10^{29} microbial cells, respectively (Wooley et al. 2010). A little information is available about the soil microbial diversity, most of which are as yet uncharacterized. Most of the microbiological research only focused on culturable microbes though based on metagenomic data soil consist of huge amount (>99%) of unculturable microbes which is yet to be discovered (Delmont et al. 2011; Pham and Kim 2012).

3 Interaction Between Soil Physiochemical Properties and Microbial Diversity

Earth is a closed system and the main source of necessary elements like hydrogen (H), oxygen (O), carbon (C), nitrogen (N), sulfur (S), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), zinc(Zn), copper (Cu), boron (B), molybdenum (Mo), nickel (Ni), etc. for all the living organisms to sustain. Soil nutritional health majorly depends upon these nutrient contents. The health of soil represents the capacity of soil to function and support the plant productivity, soil mycobiome, maintain water content, etc. (Doran 2002; Gugino et al. 2009). Soil health is directly linked to microbial diversity and composition (Fierer and Jackson 2006; Bardgett and van der Putten 2014). Soil microbiome and soil health and richness are greatly explained by soil properties. Crucial component of soil like organic matter, carbon, and nitrogen and moisture content majorly affect the microbial diversity and microbial multiplication (Chen et al. 2019; Kumar et al. 2019).

Most of the metabolic pathways in microbes are dependent on carbon compounds; therefore, microbial activity and growth are greatly affected by soil carbon concentration and other soil physicochemical properties (Meena et al. 2018; Ping et al. 2016). The nutrient concentration in the biosphere and biogeochemical cycles like nitrogen, carbon, sulfur, phosphorus, and oxygen are also greatly controlled by microbes. Carbon is a critically important element for life on the Earth and makes up most of the organic and inorganic compounds. Therefore, this is crucial to understand the complex interaction between microbial diversity and soil physicochemical properties (Deng et al. 2016; Cui et al. 2019). Environmental heterogeneity is also one of the main factors which affect the microbial biogeographic distribution and community structure. Ecosystem stability, productivity, and functioning majorly depend on biodiversity. Various advance molecular techniques like PCR and metagenomics have shown that microbial communities in different environments like terrestrial and aquatic are very dynamic and complex which is not easy to understand (Torsvik et al. 1990; Ritz and Griffiths 1994).

Soil biological function consists of all the soil microbes and organisms and their interaction with other components which is highly complex and crucial. The soil nutrient cycle or biogeochemical cycle majorly depends on metabolic processes of soil and aquatic microorganisms. The interdependence of the nutrient cycle and microorganisms is fundamental to life on this planet. Few micrograms of soil consist of thousands of microbes, and this dominating microbial diversity makes the soil a rich and biologically active ecosystem. Any of the biogeochemical cycle critically controlled by the microbial metabolic processes. Without microbes and their crucial functions, there would be no other life forms on Earth. Soil microbial communities and soil ecology functionality are directly or indirectly interconnected, and they affect each other in several ways. Change in any one's property affects each other significantly. However, soil microbial diversity also has a great impact on many soil physiochemical processes and productivity (Knelman and Nemergut 2014).

A greater understanding of soil microbial ecology and knowledge of their interactions are vital to understand soil function and sustainability. Soil ecosystem functions like mineralizing organic matter, biogeochemical cycling of carbon and nitrogen, and many other crucial processes greatly depend on soil bacterial diversity. The dominant soil microbes are *Acidobacteria*, *Actinobacteria, Bacteroidetes, Firmicutes, Proteobacteria, verrucomicrobia* and diversity of these microbes greatly change with soil biotic and abiotic factors. In spite of advance research methodologies' lack of information available on the beneficial relationships between microbial diversity and ecosystem sustainability, however, it is now well established that microbial diversity have a crucial role in the balanced functioning of biogeochemical processes at the ecosystem scale (Martiny et al. 2015). The stock of soil carbon and organic matter are greatly affected due to microbial decomposers. There is a critical interaction between soil microbial community, carbon content, and types of vegetation (Bailey et al. 2002; Meena et al. 2020; Liu et al. 2012; Deng et al. 2016). In the next sections of the chapter, main discussion will be on how soil microbial community structure influences carbon fixation and global cycling and its impact on climate change.

4 Carbon Cycle

Carbon is a critically essential and fourth most abundant six-proton atomic element in the universe and is the fundamental constituent of life on Earth. Majority of the organic and inorganic compounds on earth consist different forms of the carbon and the key molecules on Earth to support life. Earth's temperature, climate, biogeochemical cycle, energy, and global economy all are regulated by this wonder element. Carbon exit in various forms such as diamonds or graphite on Earths, but carbon dioxide (CO_2) and methane gas (CH_4) are the most primitive form of this element. Carbon molecules can exist as gases (gasoline), liquids (oil), and solids (coal) depending upon the need. Carbon is the main element for thousands of molecules like proteins, carbohydrates, lipids and nucleic acids and responsible for their structural and functional properties. On the planet carbon stored in various forms like (1) In Biosphere carbon available in the form of organic molecules, (2) In Atmospheric Carbon available in the form of carbon dioxide and methane, (3) Soil mainly consist Organic matter (4) Lithosphere consist carbon in the form of fossil fuel (5) Sedimentary rocks consist limestone, dolomite (6) Ocean sink consist carbon as dissolve carbon dioxide, calcium carbonate ($CaCO_3$). On Earth, approximately 43×10^{18} g of active carbon stock is present (atmosphere consist 750×10^{15} g; terrestrial biosphere represents 2190×10^{15} g carbon; ocean consists $39{,}973 \times 10^{15}$ g carbon) (Steele et al. 2009). Carbon concentration in the atmosphere cannot be constant; its concentration changes with the season, biological, and other anthropogenic activity. Various factors influence the carbon content in the environment like rate of photosynthesis, respiration, anthropogenic activity, microbial decomposition, etc. Rocks, sediments, ocean, atmosphere, and living organisms are the main stock points for the carbon element, whereas atmosphere serves as a Grand Central Station for the carbon. Carbon can be stored for millions of year in oceans and rocks. There are several natural mechanisms by which carbon move from one reservoir to another. The main exchange points are microbes, plants, animals, soils, sediments, and oceans. Therefore carbon keeps moving in cycle between biosphere, geosphere, and atmosphere in the form of several different types of inorganic and organic carbon compounds. Exchange of carbon between various reservoirs is called fluxes. It took seconds (e.g., universal photosynthesis process to fix atmospheric CO_2 via plant) to millennia (e.g., the carbon assimilation as in fossils) year to convert one form of the carbon to another. Carbon does not move as a single atom; instead, it binds with other elements and makes it simple to complex compounds and then move as a compound like most abundant gaseous form of the carbon is CO_2 combines with water and form carbonic acid (H_2CO_3). Further, these molecules converted into bicarbonate (HCO_3^-) and carbonate (CO^{2-}) ions or other forms to move in a cycle (Nazaries et al. 2013; Wang et al. 2016). The movement of carbon compounds between various reservoirs is called the global carbon cycle. It is operated in two phases like in Geosphere carbon cycle and Biosphere carbon cycle.

4.1 Geosphere Carbon Cycle

Geosphere consists of rocks, kerogens (petroleum and natural gas forming area), minerals, land forms of the surface and interior, abiotic (non-living), and fossils on Earth. Earth has its own carbon storage system which transfer to various other ecosystems through different processes. Geosphere comprises endogenic (upper mantle largest and greatest) and exogenic (land phytobiomass, soil humus, and oceanic biota) reservoirs of carbon (Mackenzie et al. 2004). Movement of several forms of carbon between different reservoirs can occur in short (active) and long (geologic) timescales. There is hidden cycle in deep inside earth called subduction zone where great amount of carbon stored, which significantly affect the global carbon cycle (White et al. 1970, Liu et al. 2019, Plank and Manning 2019). Geosphere carbon cycle takes a long time around thousands to millions of years. There are various chemical, physical, geological, and biological processes such as sedimentation, lithification, tectonics, metamorphism, and volcanism and metabolisms which convert carbon molecules into new forms. Sedimentary carbon includes broken remnants of living things as well as carbonate of the rocks. The organic carbon of sediments accumulates slowly through rivers with a long time. Lithosphere, which is the rocky outer part of the Earth, consist of inactive and highest carbon contents (10^{23} g C).

4.2 Biosphere Carbon Cycle

Carbon dioxide (CO_2) is the major state by which carbon entered in any biological or trophic level cycling. Photosynthesis, respiration, and combustion are the crucial bioprocesses for the biosynthesis of organic carbon compounds and conversion into new or other forms. The balancing between these processes are essential for sustainable ecosystems. In biosphere, from smallest organisms like microbes to the largest organisms like tree take part in global carbon cycling.

Therefore, biosphere can sink approximately 10% of atmospheric carbon at any given time which is just a tiny fragment of overall carbon amount. Approximately, 1.845 billion metric tons of carbon are stable in mantle and crust, whereas surface consists only 43,500 billion tons of carbon forms. Most crucial mechanisms like photosynthesis and respiration in plants and microbes regulate the global carbon cycle. Heterotrophs and autotrophs are the main components in biological carbon exchange between reservoirs. As photosynthesis fix the atmospheric carbon dioxide into organic molecules like sugars, amino acids, and lipids with the help of light energy. The second most crucial process is respiration which convert organic compounds into carbon dioxide and water and releases CO_2 back into the atmosphere and continue the global carbon cycles.

4.3 Ocean or Hydrosphere Carbon Cycle

Ocean is again a crucial carbon reservoir, and it holds about 50 times more carbon than the atmosphere. It is because CO_2 has high solubility (30 times more than oxygen) and also forms carbonate and bicarbonate ions due to its hydrolysis. These inorganic forms of carbon are utilized by marine organisms for growth and development. Carbon comes to the ocean from the atmosphere via weathering of carbonate terrestrial rocks and move through a river. The surface water plants like phytoplankton absorb CO_2 via photosynthesis process and synthesized various organic compounds. Approximately 50% of the photosynthesis mechanisms on Earth are performed by phytoplankton. The synthesized carbon via photosynthesis keeps depositing in deep carbon sinks with the gravity mechanism. Therefor net release of CO_2 from the atmosphere to the oceans and its effect on climate change is greatly influenced by the biological carbon pump. The highest carbon sink on Earth is the deep sea and its water columns. The surface organisms (phytoplankton, algae, microbes, and chemosynthetic bacteria) move carbon from the atmosphere into surface waters via various metabolic processes and then sink into the deeper ocean called a biological pump.

4.4 Global Carbon Cycle

Carbon moves globally, from one sphere to another sphere. This element presents everywhere, and it is the main component of millions of organic compounds. In any integrated ecosystem, fluxes link all kinds of carbon reservoirs to develop cycles and feedbacks. The global carbon cycle is immensely complex; it includes microbes, plants, animals, soil, ocean, sediments, rocks, etc. Following are the main steps of the global carbon cycle: CO_2, available form of carbon present in the atmosphere and efficiently absorbed by plants to carry out the photosynthesis. During photosynthesis process carbon dioxide utilised by the plant which is further converted in to carbohydrates and oxygen released to the atmosphere. It is a very crucial process to maintain the balance between carbon dioxide and oxygen concentration, and this equilibrium is the key of Earth to function.

On the ocean surface, waters near the poles absorbing more atmospheric CO_2 by phytoplankton's and microbes, where carbonate minerals like $CaCO_3$, $CaMgCO_3$, and $FeCO_3$ forms, continuously accumulate and work as a carbon sink in the ocean. Around 120,000 million metric tons carbon is fixed by photosynthesis mechanism per year, which is nearly 20 times greater than CO_2 emissions annually. Each year approximately 70% (2×10^{15} g C) of anthropogenic CO_2 is absorbed in the oceans which dissolve and mix in water. Moreover, about one third of anthropogenic CO_2 significantly assimilated in the ocean. Photosynthetic organisms like plants, algae, and microbes **flux the** carbon dioxide into sugars for energy and use for growth and development. Most of the synthesized carbon compounds enter in food chain via different links between producers and consumers like animals. Once the producers and consumers completed their life cycle, carbon return to the atmosphere due to the decomposers like bacteria and fungi via the decomposition process. Microbes use this process to synthesis the energy for microbial biomass growth and other activities (Falkowski et al. 2008). Some amount of carbon does not release back to the atmosphere eventually becoming the fossil as a fuel. Now burning of fossil fuels by a human in various activities release the carbon back to the atmosphere in various gaseous forms like CO, SO_2, NOx, VOCs, O_3, etc. Atmospheric, terrestrial, and oceanic carbon concentration significantly altered due to anthropogenic activities like burning of fossil fuels, air pollution, and deforestation. Approximately 35 billion metric tons of carbon dioxide/year added to the atmosphere due to anthropogenic activities which reached to the record 37.1 billion metric tons in 2018. Warming of surface ocean water, volcanic eruptions, and metamorphism processes also return the carbon dioxide to the atmosphere. Another least complex alkanes hydrocarbon molecule is methane (CH_4) present in atmospheric gases. The exchange of CO_2 and CH_4 between different carbon reservoirs pools significantly affect the global carbon cycle (Friedlingstein et al. 2014; Moore III et al. 2018). Methane concentration increasing drastically in atmosphere due to anaerobic-decomposition of dead natural materials, organic waste and excessive use of fossil fuels. Marshes, bogs, and deep ocean contain a great amount of methane. Most of the organic matter decay or decomposed by microbes where carbon of the biomass is converted into methane. CO_2 return to the atmosphere via oxidation of CH_4 or burning of fossil fuel hydrocarbons to obtain the energy via combustion produces (Fig. 1).

$$\text{Methane } (CH_4) + 2O_2 \rightarrow CO_2 + 2H_2O \text{ (water vapor)} + \text{heat energy}$$

5 Soil Carbon Sequestration in Plants

Sequestration of soil carbon is a long-term storage process of atmospheric carbon in soil oceans, vegetation (especially forests), and geologic formations. These carbon stocks depend on soil carbon inputs and outputs. The substantial amount of the atmospheric CO_2 exchanged between ocean, atmosphere, and land, which is quite a bigger amount than the input of anthropogenic CO_2 in the atmosphere. Approximately, 75% of the carbon pool present in soils on land, which is three times more than the amount stored in living plants and animals (Lal 2004). The sequestration process of carbon have a significant role in balancing the carbon dioxide concentration in the atmosphere and also improve the soil health via fixation of subsequent amount of carbon, which directly affects the crop yields and nutrient density. Soil carbon can be stored for millennia and released back into the atmosphere. Land and aquatic plants fix the huge amount of atmospheric carbon via photosynthesis carbon sequestration process. The captured atmospheric carbon transported to the plant root and then finally entered in the soil as available organic carbon stock. Assimilation of atmospheric carbon dioxide via photosynthesis plays a key role in the global carbon cycle and terrestrial carbon (C) sequestration. There are three important types of

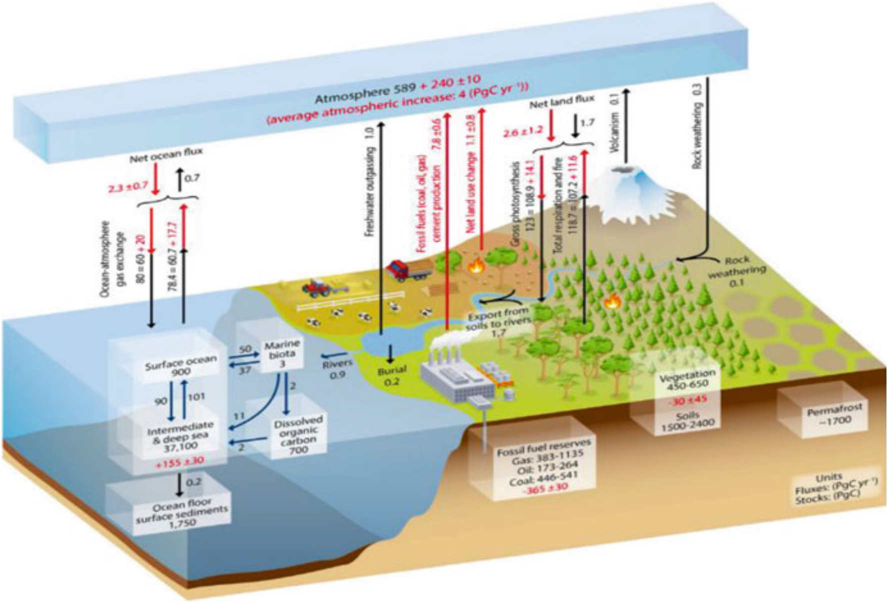

Fig. 1 A Simplified pictorial illustration of the global carbon cycle. The boxed numbers represent reservoir mass or carbon stocks in petagrams of carbon (Pg C). Arrows represent annual exchange (fluxes) in Pg C per year. Black numbers and arrows represent preindustrial reservoir masses and fluxes, while red arrows and numbers show average annual anthropogenic fluxes for 2000 to 2009. The red numbers in the reservoirs denote cumulative changes of anthropogenic carbon for the industrial period. Uncertainties are reported as 90% confidence intervals. (Adopter from Stocker et al. 2013)

carbon fixation mechanisms depending upon the processes: (i) a natural process of photosynthesis and conversion of atmospheric CO_2 into plant biomass, soil organic matter, or humus and other components of the terrestrial biosphere; (ii) involvement of engineering techniques; and (iii) those involving chemical transformations (Lal 2008). Either the simplest prokaryotic cyanobacteria or highly complex plants all follow the common mechanism for the reduction of CO_2 into various sugar-phosphate molecules.

5.1 Calvin-Benson-Bassham Cycle or C_3 Cycle or Reductive Pentose Phosphate (RPP) or Photosynthetic Carbon Reduction (PCR) Cycle

Calvin cycle is discovered about 50 years back. It is the fundamental and crucial biochemical carboxylation mechanism for the assimilation of atmospheric carbon dioxide and synthesis of sugar phosphates molecules. This pathway is popularly known as Calvin cycle (Bassham et al. 1953; Bassham and Calvin 1960). Photosynthesis is the mechanism wherein the carbon fixation process light energy converts into biochemical energy. Photosynthesis is an endothermic redox reaction. Photosynthesis reduces the carbon from OSC = +4 into the carbon dioxide OSC = +1 in the glyceraldehydes-3-phosphate (G3P), which is further used for the synthesis of sugars, amino acids, and lipids (Bleam 2017). The Calvin pathway is the primary and fundamental carboxylation mechanism in living organisms. Biological carbon fixation is a process that fix the inorganic carbon (usually CO_2) with the help of several enzymes into organic molecules (Bassham et al. 1953; Bassham and Calvin 1960).

This mechanism evolved in plants, algae, and microorganisms over billions of years ago. In the 1950s, it was generally accepted that all photosynthetic organisms used only one kind of universal pathway of photosynthesis called the Calvin cycle. For the metabolic processes reported in plant called assimilation of carbon dioxide, the Nobel Prize was awarded to the Russian-born, American scientist Melvin Calvin from the University of California, Berkeley, for his discovery in chemistry in 1961. They used radioactive carbon-14 to trace the path of carbon atoms in carbon fixation. In the Calvin pathway 5, carbon molecule converted into 6 carbon highly unstable molecule which is immediately formed very first stable compound 3-phosphoglyceric acid, which is a 3-carbon compound, so the cycle is also called as C_3 cycle and those plants follow the C_3 cycle called C_3 plant. The Calvin cycle consists of light-independent reactions or dark reaction but indirectly dependent ATP and NADPH products which synthesized in light reaction or light-dependent reaction.

Calvin cycle is a complex multistep crucial mechanism in autotrophs for inorganic CO_2 fixation in microbes and plants. Calvin cycle is found in all photosynthetic eukaryotes and most of the photosynthetic prokaryotes. In eukaryotic photosynthetic organisms, Calvin cycle takes place in the stroma. Whereas in prokaryotic photosynthetic organisms, it occurs in the cytosol. Calvin cycle is not observed in Archaea and in some obligately anaerobic and some microaerophilic bacteria. Calvin cycle is observed in diverse organisms like plants, algae, cyanobacteria, and many aerobic or facultative aerobic proteobacteria (*Rhodospirillum rubrum*), iron- and sulfur-oxidizing microbes (*Thiobacillus ferrooxidans*), green non-sulfur bacteria (*Chlorobium*), and also in some thermophiles (*Thermodesulfobium*). Calvin cycle work as an electron sink for (anaerobic) photoheterotrophic microbial growth such as some purple bacteria (e.g., *Rhodobacter*, *Rhodospirillum*, and *Rhodopseudomonas*).

The carbohydrate produced directly from the Calvin cycle is not glucose, but a three-carbon sugar: glyceraldehyde-3-phosphate. For the net synthesis of one molecule of glyceraldehyde-3-phosphate, three molecules of CO_2 are required. So the three-carbon carbohydrate precursor to glucose and other sugars via the six terminal enzymatic steps of gluconeogenesis.

The biochemical reactions of Calvin cycle occur in three different phases: (1) carbon assimilation or carboxylation phase, (2) reductive phase, and (3) regenerative phase.

5.1.1 The Carbon Assimilation or Carboxylation Phase

CO_2 is accepted by the five-carbon sugar molecule which is ribulose-1,5-bisphosphate (RuBP) and converted into a six-carbon intermediate compound which is not a stable component so it immediately splits into two molecules of a three-carbon compound, 3-phosphoglycerate (3-PGA). Therefore, 3 carbon atoms from $3CO_2$ + 15 carbon atoms from 3RuBP form 18 carbon atoms in 6 molecules of 3-PGA. In this process, inorganic form of carbon converted into organic molecules, and the process refers as carbon assimilation. The enzyme which catalyzes the first step of the cycle is (RuBP carboxylase) ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCo). It has dual nature and the tendency to bind with both CO_2 and O_2, when the concentration of carbon dioxide in the atmosphere is high, the Calvin cycle mechanism process properly. However if due to low concentration of CO_2, high temperature, and light intensity, RuBisCo bind with O_2 and then different pathway start (photorespiration instead of photosynthesis) and form phosphoglycolate which converted into glycolate. Glucose synthesized from the glycolate but utilized a larger amount of ATP energy, 2.5 ATP molecules per one molecule of O_2, which is the extra energy loss. The most abundant protein on Earth is RuBisCo which plays a crucial role in balancing the carbon cycle. RuBP carboxylase/oxygenase enzyme have dual nature, RuBP carboxylase lead the photosynthesis process and RuBP oxygenase is responsible for photo respiration mechanisms (Portis and Parry 2007).

RuBisCO is a complex molecule and comprised of both eight large subunits (catalytic) encoded by the chloroplast genome, and eight small subunits encoded by the nuclear genome form a massive hexadecameric protein structure. Activity of RuBisCo enzyme is regulated by CO_2, O_2, Mg^{2+}, and pH. Many molecules of RuBisCO require in the process because the turnover number of this enzyme is low. Approximately, three molecules of RuBP are utilized per second by the enzyme (a typical enzyme process about 1000 substrate molecules per second). Flow of carbon through the photorespiratory pathway controlled by oxygenation reaction. Several environmental variables such as high temperature and drought can increase the oxygenase reaction, and this can result in losses of between 25% and 30% of the carbon fixed. Therefore, reducing the RuBisCo oxygenase reaction has the potential to increase carbon assimilation significantly and would represent a step change in photosynthesis (up to 100% depending on temperature) (Long et al. 2006).

5.1.2 The Reductive Phase

It is the process of organic molecule reduction. During the process of carbon fixation, 3-PGA molecules synthesized, which is further converted into sugar – glyceraldehyde-3-phosphate. In case of light-dependent reactions of photosynthesis, ATP and $NADPH_2$ formed which is used in the conversion of six molecules of 3-phosphoglycerate into six molecules of glyceraldehydes-3-phosphate. This phase of the cycle is called “reduction” because both ATP and $NADPH_2$ donate the six electrons to the 3-phosphoglyceric acid to form the glyceraldehyde-3-phosphate. Both the energy molecules return back to the nearby light-dependent reactions for further utilization.

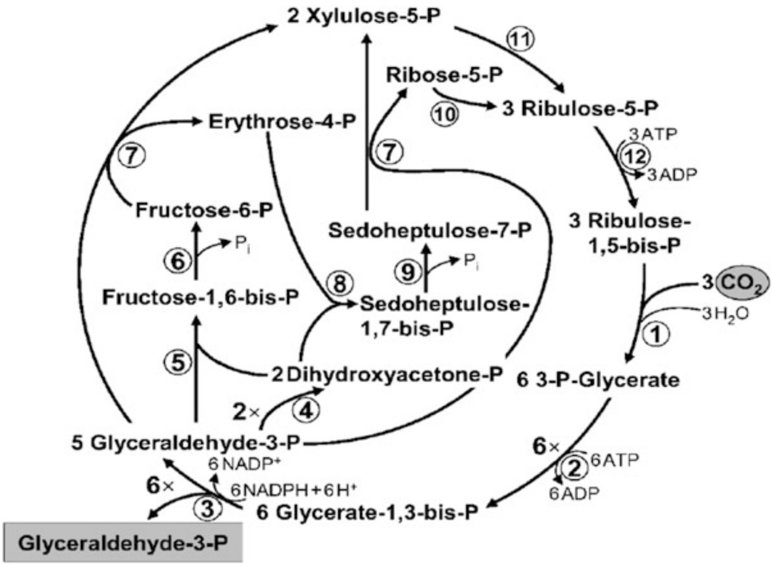

Fig. 2 The reductive pentose phosphate (Calvin-Benson) cycle. Enzymes: (1) ribulose-1,5-bisphosphate carboxylase/oxygenase; (2) 3-phosphoglycerate kinase; (3) glyceraldehyde-3-phosphate dehydrogenase; (4) triose-phosphate isomerase; (5) fructose-bisphosphate aldolase; (6) fructose-bisphosphate phosphatase; (7) transketolase; (8) sedoheptulose-bisphosphate aldolase; (9) sedoheptulose-bisphosphate phosphatase; (10) ribose-phosphate isomerase; (11) ribulose-phosphate epimerase; (12) phosphoribulokinase. (Adopted from Berg 2011)

5.1.3 The Regeneration Phase

Two molecules of glyceraldehyde-3-phosphate converted into glucose, while others utilized the light reaction product ATP and recycled to regenerate the five-carbon RuBP compound which is used to uptake new CO_2, thereby completing the cycle. The regeneration is an ATP-dependent, complex, and multistep process. The intermediates in this pathway include three, four, six, and seven carbon sugars. As in the process, one molecule glucose is synthesized by the six-carbon molecules, so the cycle has to repeat six times. Regeneration of five-carbon RuBP compound is essential in Calvin cycle to further accept new CO_2. One molecule of glyceraldehyde-3-phosphate (3 carbon) remains in the pathway as a product, and remaining five of the three-carbon glyceraldehyde-3-phosphate (total 15 carbon) are recycled back into three five-carbon molecules of RuBP. Regeneration of RuBP is an active process and used one ATP molecule. To synthesize fructose 6-phosphate or glucose 6-phosphate from CO_2, the Calvin cycle must operate six times to yield the desired hexose and reform the six RuBP molecules. The overall synthesis of Calvin cycle is one glyceraldehyde-3-phosphate and net consumption of nine molecule of ATP and six molecule of NADPH (Fig. 2).

$$3\ CO_2 + 6\ NADPH + 9\ ATP \rightarrow G3P + 6NADP + +9\ ADP$$

$$6RuBP + 6\ CO_2 \rightarrow 12\ PGA \rightarrow 6\ RuBP + \text{fructose 6-phosphate}$$

5.2 Hatch and Slack Pathway or Dicarboxylic Acid Pathway or C_4 Cycle

Till 1965, It was believed that Calvin cycle is the only pathway for CO_2 fixation in plants. Kortschak, Hart, and Burr work on sugarcane and found crucial observation about C_4 or dicarboxylic acid pathway in 1965. This observation was further confirmed by Hatch and Slack in 1967 (Hatch and Slack 1966; Graham et al. 1970; Hatch 1971, 1976). It is an alternative photosynthetic pathway of C_3 cycle to fix atmospheric CO_2, and synthesized organic molecules malate and aspartate are the crucial products of C_4 cycle. In this C_4 cycle, the first stable compound is a four-carbon organic compound which is oxaloacetic acid (OAA); therefore the name of this pathway is C_4 cycle (Furbank 2016).

The C_4 pathway is completed in two phases where two carboxylation reactions occur, one in mesophyll cells and another in bundle sheath cells (di-carboxylation pathway). The first phase takes place in the stroma of mesophyll cells, where the CO_2 acceptor molecule is three-carbon compound, phosphoenolpyruvate (PEP), to form four-carbon oxaloacetic acid. This oxaloacetic acid is a dicarboxylic acid, and hence this cycle is also known as a dicarboxylic acid pathway. The second phase of this cycle takes place in the bundles sheath cells of C_4 plant where 4 carbon compound (OAA) breaks in to 3 carbon compound (Pyruvic acid) and one carbon released in the form of carbon dioxide from this reaction which undergo in carboxylation process. The release carbon dioxide from this reaction now undergoes carboxylation process. Open and arid high-temperature habitats are dominated with C_4 plants like maize, sugarcane maize, and sorghum and in many grasses like kangaroo grass, red grass, and wiregrass. C_4 plants have great adaptive mechanisms which is not available in C_3 plants at high temperature and harsh environmental conditions or under strong light because C_4 cycle in C_4 plant has a reduction or absence of photorespiration, with efficient rates of CO_2 fixation. Additionally, two extra molecules of ATP required in C_4 plants to fix one molecule of CO_2. C_4 plants have higher growth rate in subtropical and tropical environments because of their excellent efficiency in photosynthetic pathways. The C_4 plants show specific feature in leaf anatomy, as chloroplasts are dimorphic and bifunctional (Leegood 2002; Furbank 2016). The vascular bundle sheath cell of C4 plants are surrounded by a larger number of parenchymatous cells. These bundle sheath cells have great numbers of chloroplasts and a large amount of RuBisCo, which is fully protected from O_2.

This specific kind of anatomy of leaves in C_4 plants is called Kranz anatomy, (Kranz in German means wreath). Basically, the C_4 pathway is a cyclic process and completed in the following four steps: (1) carboxylation, (2) breakdown, (3) splitting, and (4) phosphorylation.

5.2.1 Carboxylation

Carboxylation takes place in the chloroplasts of mesophyll cells, where three-carbon molecule phosphoenolpyruvate (PEP) accept the atmospheric CO_2. The enzyme that catalyzes this CO_2 fixation is PEP carboxylase or PEPcase. The maximum amount of ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCo) enzyme present in bundle sheath cells and mesophyll cells of C_4 plants consist less quantity of this enzyme. Phosphoenolpyruvate, a three-carbon compound present in mesophyll cell, accepts the atmospheric CO_2 and forms a four-carbon oxaloacetate compound in the presence of water. This reaction is catalyzed by the enzyme, phosphoenolpyruvate carboxylase.

5.2.2 Breakdown of (OAA)

The four-carbon oxaloacetic acid (OAA) which is formed in the mesophyll cells is broken down into again four-carbon malate and aspartate in the presence of the enzyme, transaminase, and malate dehydrogenase. The breakdown of OAA takes place in the mesophyll cells; these four-carbon molecules are then transported to the bundle sheath cells. The bundle sheath cells are rich in an enzyme RuBisCO but lack PEPcase, CO_2, and O_2.

5.2.3 Splitting

In the bundle sheath cells, four-carbon molecules malate and aspartate converted into pyruvate (three-carbon compound) and so release the one molecule of carbon dioxide in the presence of enzymes (decarboxylases: NAD- and NADP-malic enzymes and PEP carboxykinase). The free CO_2 accepted by the RuBisCo in completion of Calvin's cycle in the sheath cell. This is the second carboxylation occurs in the chloroplast of bundle sheath cells. Here CO_2 is accepted by five-carbon compound ribulose-1,5-bisphosphate in the presence of the enzyme and carboxy dismutase and ultimately yields 3-phosphoglyceric acid. Some of the 3-phosphoglyceric acid is utilized in the formation of sugars, and the rest regenerates ribulose-1,5-bisphosphate.

5.2.4 Phosphorylation

The pyruvate molecule now transports to the mesophyll cell and phosphorylated to resynthesize the phosphoenolpyruvate in the presence of ATP, and the reaction is catalyzed by pyruvate phosphokinase. C_4 cycle is the adaptation mechanism available in C_4 plants that overcomes the limitation of the photorespiration, enhanced photosynthetic efficiency, and minimizing the water loss in hot and dry environments (Matsuoka et al. 2001; Nazaries et al. 2013). Mostly the plant species which consists C_4 cycle originate from warmer climates. Several tropical and subtropical grasses and some dicots dominantly show the CO_2 fixation through C_4 cycle. More than thousands of species are discovered for C_4 cycle. Approximately 300 species belong to dicots, and the rest of them are monocots. 5% of Earth's plant biomass are represented by C_4 plants and 1% of its known plant species. Although C_4 cycle are represented by fewer numbers of plant diversity, they are highly efficient and fix more than 20% of terrestrial inorganic carbon. Enhancing the diversity of C_4 plant on Earth could help in more CO_2 bio sequestration and could be crucial way in climate change strategy. Hatch and Slack pathway is the combined pathway of C_3 and C_4 cycles of carboxylation and both the cycle linked due to the specialized leaf Kranz anatomy. C_4 plants consist dimorphic and bifunctional chloroplasts there for these plants are highly efficient for photosynthesis mechanism as compare to the C_3 plants (Hodge et al. 1955; Langdale 2011). The biochemical reaction of C_4 plants is not so unique; most of these reactions occur in C_3 plants because they may not be used primarily in photosynthesis. C_4 plants have specific proteins (encoded by are encoded by multigene families) to function at a specific time and conditions and then enhance production (Hibberd and Covshoff 2010; Kellogg 2013). Another fact is that phosphoenolpyruvate carboxylase enzyme of C_4 plants have more affinity for CO_2 than the ribulose bisphosphate carboxylase of the C_3 cycle for the atmospheric CO_2 fixation in organic compound during carboxylation. Although the C_4 cycle is more efficient, only a small portion of the world's plant species fix the CO_2 through C_4 cycle. Approximately 3% of the vascular plants fix the inorganic CO_2 through C_4 cycle and contribute around 20% to the global primary productivity on lands (Ehleringer and Monson 1993; Ehleringer et al. 1997). Thus all these specification make C_4 pathway a more efficient metabolism as compared to C_3 cycle (Lara et al. 2002; Lara and Andreo 2005).

5.3 Crassulacean Acid Metabolism (CAM) Pathway

Approximately 40% of the total surface area of the Earth represent arid and semiarid ecosystems. CO_2 fixation mechanism in plants growing in arid region has to face various challenges like limited opening of stomata so less supply of carbon dioxide from the air. Arid environments are extremely diverse in terms of their land forms, soil, fauna, flora, temperature, and less water availability. The less rainfall and high temperatures in such areas increase the water evaporation. The plant diversity growing in such harsh environment develops the acclimatization mechanisms against the drought, long exposure to high UV radiation, high temperature, and poor nutrient availability in the soil. Several plant species can grow under such harsh environmental conditions like Agavaceae and Cactaceae, both of these are taxonomically unrelated plant families.

The drought-resistant plants consist of Crassulacean acid metabolism (CAM), a specialized mode of photosynthesis machinery which was first discovered in members of plant family Crassulaceae that's why it is called Crassulacean acid metabolism (CAM) pathway (Bräutigam et al. 2017). CAM plants have scotoactive stomata (active during night) which accept free atmospheric CO_2 during the night for carbon assimilation. In such plants gases exchange specially at night when air temperature comparatively low with less water vapor pressure, this way is significantly decrease the evaporation of water during day time and also improve the water-use efficiency (WUE). Such specific mechanisms increase the adaptability of plants to hotter and drier climates.

CAM plants also consist of specific cell anatomy such as succulence at the cellular level (large thin-walled vacuoles for the storage of water and organic acids) as well as with succulence in leaves, stems or pseudobulbs, thick cuticle, and superficial and contractile roots. These physiological features of succulent plants help them to survive in arid ecosystems where poor water level and comparatively high temperatures. These inorganic CO_2 molecules encounter hydroxyl ions OH- and form carbonic acid. The HCO_3 then react with phosphoenolpyruvate (PEP) and formed oxaloacetate with the help of phosphoenolpyruvate carboxylase enzyme. Oxaloacetate then receives an electron from NADH and formed the malic acid (night acidification); this reaction is catalyzed by the enzyme malate dehydrogenase (MDH). Malic acid accumulates in plant cell vacuoles till sunrise, and then during day deacidification, the malate breaks into pyruvate, and released CO_2 is incorporated by RuBisCo in the Calvin cycle for the complete carbon fixation (Silvera et al. 2010). RuBisCo molecules have lower affinity for CO_2 than PEPcase, and it is light dependent. CO_2 concentration in CAM plant photosynthetic tissues is relatively high. Once RuBisCo is active, the reduction in photorespiration is higher as compare to C_3 plants. CAM plants consist long-term water use efficiencies (10–40 g CO_2 fixed per kg H_2O transpired) which are correspondingly higher than in C_3 or C_4 plants. Approximately 10% of vascular plants represent CAM photosynthesis pathway. Malate is the crucial molecule of this pathway, and it can be stored in vacuole. As in C_4 plants, CAM also represents a variation in biochemical pathways and evolved many.

6 Role of Microbes in Carbon Fixation

Carbon is the building block of all the life forms on mother earth and the main element of the Earth crust. Each simple or complex molecules like proteins, nucleic acid, carbohydrate, lipids, etc., always consists of carbon atoms bonding with other elements like oxygen, hydrogen, nitrogen, phosphorus, etc.; these carbon-based compounds provide the materials and energy for the metabolism of living organisms to survive and ecosystem function. In atmosphere, carbon exists in several forms of organic and inorganic molecules. On Earth, carbon found in three different forms called allotropes and allotropes of carbon can be either amorphous or crystalline diamond, graphite, and fullerenes. The atmospheric CO_2 concentrations greatly regulated by soil carbon and the biggest carbon sink in the terrestrial biosphere is soil organic carbon (SOC) which is microbially decomposed and release approximately 60–110 Pg carbon dioxide to the environment (Bond-Lamberty and Thomson 2010; Schmidt et al. 2011; Ciais et al. 2013; Wang et al. 2017).

Carbon fixation is also referred to as carbon assimilation, which carried out due to conversion of carbon dioxide to an organic compound by the various living organism like plants, phytoplanktons, and microbes. As we have discussed earlier, plant fixed the atmospheric carbon dioxide and release it into the soil which become the main carbon source for the microorganisms (Luo et al. 2014). The released stock of C exudates into the soil depends on root fluxes, adsorption of soil mineral, diffusion across soil pores, mineral fixation in soil, and microbial utilization (Kuzyakov et al. 2003). Microorganisms utilize the fixed carbon from plant biomass or CO_2 release at the time of microbial decomposition of organic matter. So, like plant carbon assimilation, various microorganisms also play crucial role in transformation inorganic carbon dioxide to organic biomass. Microorganisms play key role in carbon fixation and they change their strategies to deal with variation in carbon concentration. Microorganisms like cyanobacteria (*Synechococcus elongatus*), green algae

(*Chlamydomonas reinhardtii*, *Chlorella vulgaris*, and *Nannochloropsis gaditana*), and some autotrophic bacteria (*Chlorobium limicola*, *Clostridium aceticum*) are more efficient CO_2 fixer as compared to the plants due to their faster growth (Jones 2008; Berg et al. 2010; Adamczyk Michałand Lasek and Skawińska 2016; Branduardi and Sauer 2017; Zhang et al. 2017).

During microbial metabolism, microorganisms use organic C substrates for respiratory energy production and biosynthetic stabilization involving cell maintenance and growth. Conversion process of inorganic carbon into organic material have key role in biological evolution. The ratio of growth, development and fixation of the carbon called carbon use efficiency (CUE) which determining the stock of carbon in soil during decomposition process (Manzoni et al. 2012). Microbial CUE can be affected by environmental factors such as resource availability, stoichiometry, microbial physiological activity, metabolic pathways and the composition of the microbial community, and some external factors such as temperature, moisture, pH, etc. (Manzoni et al. 2012; Roller and Schmidt 2015). In the rhizospheric region, CUE is altered with plant-microbial interactions and microbial metabolism. Microbial CUE values vary in different habitats like terrestrial and aquatic. For aquatic microbes, CUE values present in the range of 0.05 to 0.60 (del Giorgio and Cole 1998) and for soil microbes CUE calculated within the range of 0.30–0.55 (Sinsabaugh et al. 2013, 2016). In non-rhizospheric soil microbes, CUE is 1.5 times higher than in the rhizospheric soil (Blagodatskaya et al. 2014). Carbon containing molecules and plant biomass positively related to microbial growth and community composition. The diverse environment sites consist different nutrient complex molecules which is fixed by the functionally diverse microbes to enhance the plant biomass and directly or indirectly affect the nutrient pool on earth (Sharma et al. 2011; Sharma et al. 2016). In 1940's various scientific studies been conducted to explain microbial carbon fixation process (van Niel 1932; Wood and Werkman 1938; Wood 1991).

Based on recent studies, it is now well established that CO_2 assimilation is a common mechanism in various microbes like photoautotrophic and chemolithotrophic, photosynthetic and non-photosynthetic (dark anaplerotic), and aerobic and anaerobic. All the autotrophs can utilize the inorganic substances like reduce carbon dioxide and fix it to make organic compounds for biosynthesis and create a store of chemical energy.

Broadly, organisms can be split in two categories: one autotroph, like plants, which synthesize their own food from inorganic materials like light and carbon dioxide and form most of the Earth biomass, two heterotrophs, like animals and some forms of heterotrophic microbes, which rely on gobbling up other organisms and organic compounds to survive. Further, autotrophs are of two types: the photoautotrophs use light energy; chemoautotrophs use chemical energy. Chemoautotrophs like *Bathymodiolus*, *Alviniconcha*, *Thiobacillus thiooxidans*, and *Mariprofundus ferrooxydans* also play very important role in CO_2 fixation because several ecosystems like deep-sea vents are dependents on CO_2 fixation by free-living or symbiotic chemoautotrophs. These organisms take the inorganic carbon and water and synthesized the organic compounds with the help of energy obtained through the

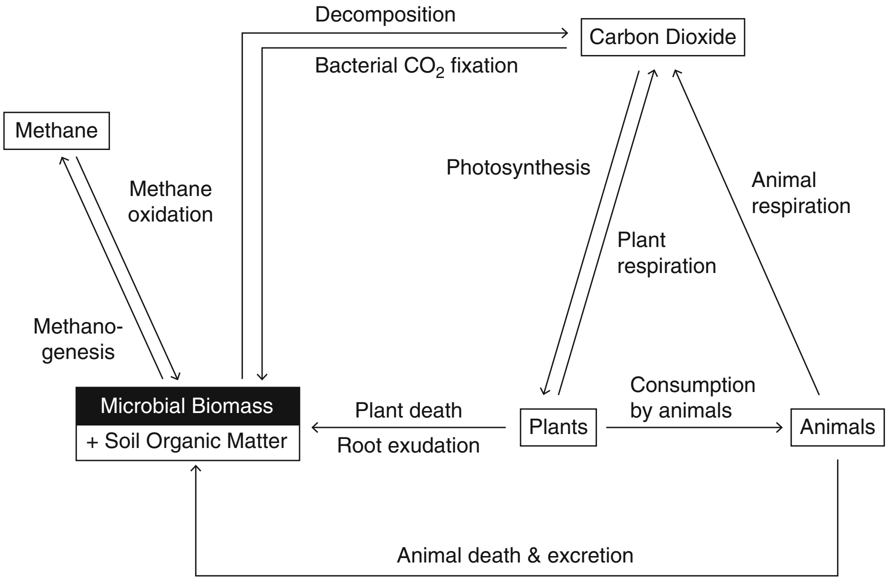

Fig. 3 Carbon cycle followed on terrestrial by soil microorganisms. (Adapted from Prosser 2007)

oxidation of reduced compounds. Inorganic CO_2 fixation in anoxygenic phototrophs known as purple non-sulfur bacteria (PNSB) plays key role in maintaining redox homeostasis balance (Richardson et al. 1988; Shively et al. 1998).

PNSB use light, carbon, and organic substances to synthesis energy for their growth under anaerobic conditions called photoheterotrophic growth. Autotrophic and heterotrophic organisms follow a variety of different pathways like decomposition of organic material and then returned the fixed carbon back to the atmosphere. Slow rate of organic matter decomposition decreases the return rate of CO_2 back to the atmosphere and directly minimize the soil disturbances and increased soil carbon stability. Several studies show that carbon stock in soil depends on microbial diversity, growth rate, and their metabolic process. If the return rate of CO_2 back to the atmosphere is high, it affects the global warming and climate change. Existing environmental issues again exacerbated due to increase in climate change caused by combustion of organic matters, rising the pollution levels of carbon dioxide in the atmosphere. Therefore, it is very crucial to control the CO_2 emission levels or to reduce atmospheric carbon dioxide by different physical, chemical, and biological methods (Allen et al. 2009; Ekwurzel et al. 2017). Figure 3.

Microbial CO_2 fixation produces huge amount of organic biomass which can be used further for bioenergy production like biofuel. Also, microbes ferment and decomposed the plant carbohydrates and plant biomass to produce biofuels. Microbial and plant biomass can solve so many environmental issues like global warming and climate change (Shively et al. 2001).

6.1 Mechanisms of CO_2Fixationin Microbes

6.1.1 Autotrophic CO_2Fixation

Fixation of inorganic carbon into organic carbon is the life-sustaining process on Earth. CO_2 fixation earlier is reported in plants, but later it is also discovered in cyanobacteria (blue-green algae) and some bacteria such as free-living autotrophs, symbiotic autotrophic bacteria, and chemoautotrophic bacteria. Organisms use light as energy source to produce ATP to preform various cellular and metabolic processes called photoautotrophs and photoheterotrophs. These organisms utilize the sunlight, atmospheric carbon dioxide, and water to perform photosynthesis and synthesize organic materials for the cellular growth and function like respiration. Photoheterotrophs are the organisms dependent for their growth and development on organic matter produced by other living beings. Photoheterotrophs also use sun light as an energy source and organic material synthesized by other organism source as carbon.

6.1.2 Chemoautotrophs CO_2 Fixation

Chemoautotrophic organisms derive their energy for metabolic activity through the photophosphorylation of various inorganic or organic food substances in their environment. Chemoautotrophic bacteria are of two types: obligate chemoautotrophic bacteria (completely dependent on CO_2 fixation mechanism for their life) and facultative chemoautotrophs (utilized organic molecules synthesized via Calvin cycle and also have ability to use a other growth substrates). *Betaproteobacteria* and *Gammaproteobacteria* (*Thiobacillus* and *Thiomicrospira*, respectively) are the most common type of facultatively chemoautotrophic bacteria; these microbes have different types of metabolic processes to utilize wide range of substrate for survival (Ghosh and Dam 2009).

6.2 Chlorophyll-Based Bacterial Photosynthesis

Oxygenic and anoxygenic photosynthesis are the chlorophyll-based bacterial photosynthesis like in *Cyanobacteria*, *Proteobacteria*, *Chlorobi*, *Firmicutes*, *Acidobacteria*, *Gemmatimonadetes*, and *Chloroflexi* (Fischer et al. 2016). There are three different categories of CO_2 fixing bacteria via photosynthesis: purple phototrophic bacteria, green bacteria, and the cyanobacteria.

6.2.1 Purple Phototrophic Bacteria (PPB)

Purple phototrophic bacteria have efficient photosystem composed of carotenoids and bacteriochlorophylls, which can use infrared light (IR) as the main energy source for carbon fixation. These microbes are most multifaceted anaerobic facultative microorganisms. PPB are of two types: purple non-sulfur bacteria (PNSB) such as *Rhodobacter sphaeroides*, *Rhodopseudomonas viridis*, *R. palustris*, *Rhodospirillum rubrum*, *etc*, and purple sulfur bacteria (PSB) like *Chlorobium thiosulfatophilum* and *Chromatium vinosum* (Pfennig 1967; Sirevåg and Ormerod 1970).

Purple phototrophic bacteria perform anoxygenic kind of photosynthesis as sun light is captured and synthesized the high energy molecule ATP without production of oxygen. In such kind of photosynthesis, water is not used as an electron donor. In case of purple sulfur bacteria, H_2, H_2S, and S work as photosynthetic electron donor, whereas in purple non-sulfur bacteria mostly organic molecules, nitrite and H_2. These microbes have only one type of reaction center similar to plant photosystem II. Purple sulfur and non-sulfur bacteria mainly contain bacteria chlorophyll a or bacteria chlorophyll b pigments. PPB have well-developed metabolic system to fix C, N, S, P, and Fe via various pathways and efficiently accumulate the organic nutrients (Batstone et al. 2015). These microbes can extract crucial products from waste materials such as biofuels like bio-hydrogen, bioplastics as polyhydroxyalkanoates and polyhydroxybutyrate (PHA, PHB), and single-cell proteins; therefore PPB are great source for alternative fossil fuels.

6.2.2 Green Phototrophic Bacteria (GPB)

GPB are phylogenetically different unicellular anaerobes with unique light harvesting chlorophyll (bacteriochlorophyll and carotenoids). GPB chlorophyll is different as it contains vesicles that are attached with the inner face of the cytoplasmic membrane called chlorosomes. GPB are of two types: filamentous green non-sulfur bacteria (e.g., *Chloroflexus aurantiacus*, *C. aggregans*) and green sulfur bacteria (e.g., *Chlorobium thiosulfatophilum*, *C. phaeobacteroides*, and *C. limicola*) (Zarzycki et al. 2009). Both kinds of bacteria use CO_2 as sole carbon source and consist of large amount of bacteria chlorophyll c and less amount of bacteria chlorophyll a. Some of the green sulfur bacteria also consist of bacterial chlorophyll c, d, or e organized in the form of an aggregate. In case of green sulfur bacteria H_2, H_2S, and S work as photosynthetic electron donor, whereas in green non-sulfur (gliding) bacteria, mostly various sugar molecules, amino acids, organic acids, and H_2 work as photosynthetic electron donor. GPB basically contains only single type of reaction center present in the cytoplasmic membrane which is very much similar to the plant photosystem I.

6.2.3 Cyanobacteria

Earlier in 1974, cyanobacteria used to call as blue-green algae. Among bacteria, *oxygenic photosynthesis* is performed only by cyanobacteria. Oxygenic photosynthesis is a non-cyclic photosynthetic electron chain where water works as electron donor and generates molecular oxygen as by-product during photosynthesis. Similar to the plants, cyanobacteria have two reaction centers photosystem I and photosystem II. In cyanobacteria key mechanism for the synthesis of organic matter is only oxygenic photosynthesis. Cyanobacteria consist of chlorophyll a as a main photosynthetic green pigment, but also consist of accessory blue and red phycobilin pigments (phycocyanin and phycoerythrin, respectively) and yellow photosynthetic pigments like carotenoids. These pigments allow cyanobacteria to utilize the orange and green regions of the light spectrum.

6.3 Non-chlorophyll-Based Bacterial Photosynthesis

Some of the bacteria like archaea use bacteriorhodopsin in place of chlorophyll to capture the sun light. Bacteriorhodopsin (bR) a purple pigment, is an integral transmembrane bound protein work as a light-driven proton pump which convert light energy to chemical energy like ATP for cellular growth and function (Jin et al. 2006; Berg et al. 2010). This protein form two-dimensional crystalline patches which can occupy up to nearly 50% of the surface area of the archaeal cell. One of the best archaeon is *Halobacterium salinarum* which have bR. Two distinct components, chromophore (wavelength 405–790nm) and retinal present in bR which capture the green light (wavelength 500–650 nm) there after protons start moving across the plasma membrane to the periplasmic space. So this light-driven proton pumping generates a pH gradient that can be used to synthesis of ATP by a chemiosmotic mechanism (Haupts et al. 1999). This mechanism is quite similar to the pigment rhodopsin found in the vertebrate retina.

7 Pathways for CO_2 Fixation in Microbes

Till date, six different pathways are discovered in prokaryotes for atmospheric carbon dioxide assimilation. The most common pathway in plants and microbes is Calvin-Benson-Bassham cycle or Calvin cycle. However, five alternative pathways are also available in various microbes, and these pathways are reductive acetyl-coenzyme A pathway, reductive citric acid cycle, dicarboxylate/4-hydroxybutyrate cycle (DC/HB), hydroxypropionate/4-hydroxybutyrate cycle (HP/HB), and 3-Hydroxypropionate bicycle.

7.1 Calvin-Benson-Bassham Cycle or Reductive Pentose Phosphate Cycle or C3 Cycle or Photosynthetic Carbon Reduction (PCR) Cycle

Calvin cycle of Co2 fixation is common in both plants and microbes which is discussed in Sect. 5.1.

8 Alternative CO_2 Fixation Pathways

Earlier it was believed that the Calvin-Benson cycle is the only CO_2 fixation pathway present in plant and microbes. But now it is not the only option, following five well-defined alternative pathways also available in microbes (Preuß et al. 1989; Hügler and Sievert 2011).

8.1 Reductive Acetyl-Coenzyme a Pathway or Wood-Ljungdahl Pathway

The acetyl coenzyme A (CoA) pathway or the reductive acetyl-CoA is one of most diverse carbon fixation biochemical pathways utilized for energy conversion by bacteria in anaerobic conditions. The reductive acetyl-CoA pathway commonly called as Wood-Ljungdahl pathway, it was discovered in 1986, in the research laboratories of Harland G. Wood, Lars G. Ljungdahl and Thauer. This pathway mostly used by acetogens (*Clostridiales* and some *Spirochete*), sulfate-reducing autotrophic bacteria (SRB), aceticlastic methanogens, and syntrophic acetate-oxidizing bacteria (SAOB) and psychrophilic or thermophilic bacteria to synthesize acetyl-CoA from CO_2 (Schäfer et al. 1999; Drake et al. 2008; Wiechmann and Müller 2017; Schönheit and Schäfer 1995).

Autotrophic acetogens (e.g., *Moorella thermoacetica*) and methanogens (*Methanomassiliicoccales*) synthesize acetic acid and CH_4 from CO_2 by using this complex pathway. Most of these microbes synthesized approximately 10 trillion kilograms of acetic acid every year, which is very crucial in the global carbon cycle and another biogeochemical cycle. Reductive acetyl-CoA pathway is very much different from the other mechanisms like Calvin-Benson cycle and reductive citric acid cycle due to its noncyclic carbonic fixation where acetyl-CoA synthesized from CO_2. In this cycle regeneration of the primary CO_2 acceptor is absent. However, the reductive acetyl-CoA cycle uses hydrogen atoms as an electron donor and carbon dioxide as an electron acceptor and produces acetyl-CoA as the final product. Acetyl-CoA is a very crucial compound in various metabolic processes and used in many biochemical reactions such as the citric acid cycle. The acetyl-CoA pathway starts with the reduction of two molecules of CO_2 in parallel to form acetyl-CoA. In case of first CO_2 molecule reduction, a methyl radical formed which bound to a tetrahydropterin coenzyme, whereas the second CO_2 molecule first reduced to carbon monoxide which combines with the nickel radical in the reaction center and releases coenzyme A to form an acetyl-CoA molecule.

The reductive acetyl-CoA consists of two CO_2 entry branch points: the methyl-branch point or Eastern branch point and the carbonyl-branch point or western branch point. In this pathway, two reaction oxidation and reduction of two molecules of carbon dioxide start simultaneously. At the methyl-branch, CO_2 turns into methyl-group (methyl-H_4F in case of acetogens or methyl-H_4MPT, in case of methanogens). At the carbonyl-branch, CO_2 first reduced into carbon monoxide (CO) and then combined with the methyl group and coenzyme A (CoA) and finally acetyl-CoA (Ragsdale and Pierce 2008; Thauer 2007a; Berg et al. 2010; Fuchs and Berg 2014).

The reductive acetyl-CoA pathway is regulated by two crucial enzymes carbon monoxide dehydrogenase and acetyl-CoA synthetase. The organisms produce carbon monoxide dehydrogenase enzyme that help them to uptake carbon dioxide as a source of carbon and carbon monoxide as a source of energy. This enzyme combined with acetyl-CoA synthase and methyl group and then form a complex which is crucial for the acetyl-CoA pathway for the synthesis of acetyl-CoA. The acetyl-CoA

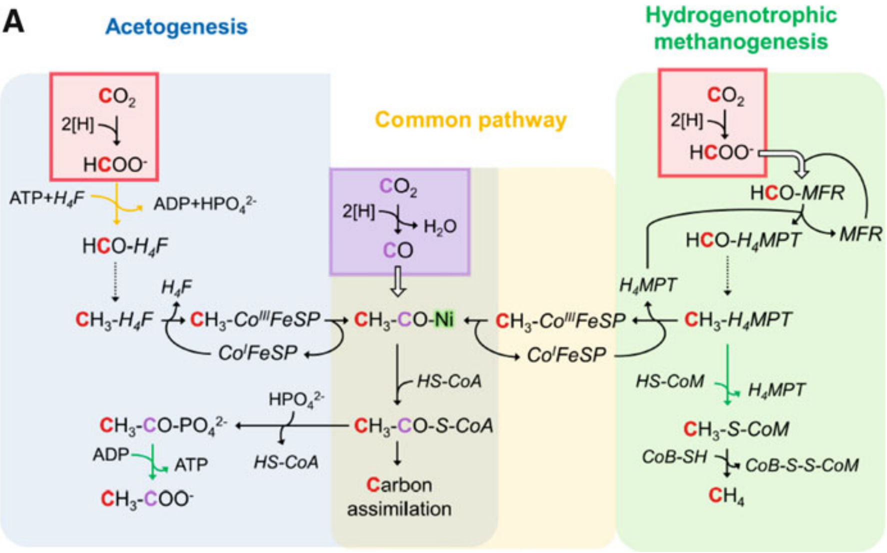

Fig. 4 Variations in the reductive acetyl-CoA pathway between acetogenic bacteria and hydrogenotrophic methanogens, implicated active sites and mechanisms. (A) Differences in the reductive acetyl-CoA pathway between acetogenic bacteria (left and middle) and methanogenic archaea (right and middle). Acetogens and methanogens share a conserved "carbonyl" branch (common pathway) used to build biomass for both and to conserve energy for acetogens. The green arrows correspond to reactions coupled to energy conservation (ATP or electrochemical ion gradient generation across the membrane) and the orange one to ATP hydrolysis-coupled reaction. Dashed arrows correspond to three successive reactions: dehydration and two reduction steps. White arrows indicate the usage of an internal channeling system between two active sites. Red and purple squares highlight CO_2-reduction events, in red Fdh reaction and in purple the CODH reaction. The ACS contains the A-cluster harboring the binuclear nickel center highlighted by a green glow. The cofactors involved in these processes are tetrahydrofolate (H4F), tetrahydromethanopterin (H4MPT), coenzyme A (CoA-SH), methanofuran (MFR), reduced/oxidized corrinoid FeS containing protein (CoI/CH3-CoIII-FeSP), coenzyme B (CoB-SH), and coenzyme M (CoM-SH). (Adapted from Lemaire et al. 2020)

may be carboxylated to yield pyruvate, which can then be converted to glucose and other organic compounds or precursor metabolites (Fig. 4).

Clostridium thermoaceticum bacteria were used as a model organism to understand the several steps involved in this mechanism. *Clostridium thermoaceticum* is an obligate anaerobe, Gram-positive, spore-forming, rod-shaped, thermophilic bacteria which can grow at 55–60 °C temperature and 6.6–6.8 pH. During fermentation, *Clostridium thermoaceticum* utilize the one mole of glucose and produce 2.5 moles of acetic acid. *Acetogens* and *Methanogens* are the crucial organisms that assimilate CO_2 through reductive acetyl-CoA pathway.

8.1.1 Carbonyl or Western Brach Point

In this branch, the first step is that one molecule of carbon dioxide reduced to carbon monoxide or carbonyl group with the help of carbon monoxide dehydrogenase (CODH), carbonyl group again combined with CoA, and a methyl group (from western branch) to form acetyl-CoA with the help of catalyst acetyl-CoA synthase (ACS) complex CODH/ASC is the key enzyme for the regulation of this pathway.

8.1.2 Methyl or Eastern Branch Point

In the methyl branch where a reductive cascade turns carbon dioxide into methyl group of an acetate molecule. This is also a multistep process and completed with the help of various enzymes and cofactors. First, CO_2 is reduced to formate and the reaction catalyzed by NADPH-dependent formate dehydrogenase (FDH). NAD +- -dependent formate dehydrogenase (FDH) is an abundant enzyme and first purified by Andreesen and Ljungdahl from *Clostridium thermoaceticum*. Formate dehydrogenase (FDH) plays crucial role in energy supply of methylotrophic microorganisms and also reported in plants under stress. Now, formate utilized the ATP molecule for its activation then bound to tetrahydrofolate (H_4F) and yielding formyl-H_4F with the help of oxygen stable monofunctional enzyme formyl-H_4folate synthase. Then the formyl-H_4folate is converted into methenyl-H_4folate with the help of methenyl-H_4folate cyclohydrolase and here one molecule of water release. Methenyl-H_4folate undergo reduction and form methylene-H_4folate, which is further reduced into methyl-H_4folate through the enzyme methylene-H_4folate dehydrogenase and methylene-H_4folate reductase, respectively. In the next step, water is split off and used by methylene-H_4Folate, and then the methenyl group is reduced to methyl-H_4F for acetogens or methyl-H4MPTor methanogens. Now methyl group is accepted by the carrier protein which consists a corrinoid cofactor, tetrapyrrolic corrin ring, with cobalt at the center and contains iron-sulfur clusters. Therefore the name of this protein is an iron-sulfur protein (CFe-SP). The molecular mass of this protein is 88 kDa (subunits α -55 kDa and β -33 kDa) which is purified from *C. thermoaceticum*. Methyl group is crucial here, which is condensed on bifunctional CO dehydrogenase/acetyl-CoA synthase (CODH/ACS) to form acetyl-CoA. Acetyl-CoA is catalyzed by phosphotransacetylase and acetate kinase to synthesized acetate and release on ATP molecule. During this process, one mole of ATP is produced by SLP (substrate level phosphorylation) in the acetate kinase reaction. In this pathway, the net ATP gain by SLP is zero because one mole of ATP is consumed during the synthesis of formyl-H_4F with the help of synthetase. Based on various research on bioenergetic, acetogens are further divided into two groups: the Na^+-dependent acetogens with *Acetobacterium woodii* and the H^+-dependent acetogens with *Moorella thermoacetica* formerly called *Clostridium thermoaceticum.* The whole-genome sequencing analysis of C. *thermoaceticum* gave a view of the genes involved in this pathway (Ragsdale and Pierce 2008). The genes for the enzymes involved in methyl branch are scattered all over the bacterial genome. In contrast, genes of enzyme involved in the western branch are grouped in an ACS gene cluster which encodes four crucial enzymes of the pathways, i.e., CODH, ACS, two subunits of CFe-SP, and methyltransferase (MeTr) (Fig. 4).

8.1.3 In the Case of Methanogens

They can convert compounds such as CO, CO_2, and H_2, formate, methylamines, methanol, and acetate to methane. Methanogens use highly efficient CO_2 as a substrate and H_2 as electron donor hydrogenotrophic methanogenesis.

In the first step, formyl-methanofuran formed after the reduction of CO_2 with the help of formyl-methanofuran dehydrogenase (F_{wd}) catalyzing complex. In this step reduced ferredoxin (Fd_{red}) is the electron donor. Two isoforms of formyl-methanofuran dehydrogenase are present in microbes molybdenum- or tungsten-dependent formate dehydrogenase (Wagner et al. 2016). In the second step, the tetrahydromethanopterin (H_4MTP) molecule accept the formyl group and form formyl-H_4MTP. Then the formyl group undergoes dehydration and reduction process and form methylene-H_4MTP and subsequently to methyl-H_4MTP (methyltetrahydromethanopterin -CH_3H_4MPT). In this process, reduced F_{420} ($F_{420}H_2$) work as an electron donor. The methyl-H_4MPT develop a cross-link between carbon assimilation and energy conservation (Schäfer et al. 1999). The methyl group from methyl-H_4MPT is then transferred to coenzyme M (HS-CoM). Finally, methyl-CoM is reduced to methane with coenzyme B (HS-CoB) as an electron donor. The resulting coenzyme-B heterodisulfide (CoM-S-S-CoB) is reduced with H_2 to recycle the coenzymes (Thauer 2007b). It is also important to note that several methanogens can use formate instead of H_2 as electron source for CO_2 reduction.

8.1.4 *Acetogens*

Acetogens are specialized anaerobic prokaryotes group ubiquitous in nature. Acetogens use the "Wood–Ljungdahl" mechanism for production acetate from the inorganic CO_2 reduction. These bacteria follow the "Wood-Ljungdahl" pathway for (a) acetyl-CoA synthesis from CO_2, (b) conservation of energy, and (c) production of biomass due to assimilation of CO_2. Such kind of metabolic capability to synthesized acetate differentiates acetogens from other organisms and the process used for acetate synthesis is known as acetogenesis. Acetogens play a crucial role in global carbon cycle as they produced tons of acetate each year via acetogenesis (Ljungdhal 1986; Ragsdale and Pierce 2008; Lemaire et al. 2020). Acetogens are highly diverse, and more than 19 genera have been described till date. Acetogens utilized various molecules like H_2-CO_2, CO, or formate and form acetate. Acetogens are highly diverse; around 19 bacterial genera have been described to date.

8.1.5 Methanogens

Methanogens are also a phylogenetically diverse group of strictly anaerobic Euryarchaeota. Methanogens have specific energy metabolic process for the production of methane from CO_2 and H_2, formate, methanol, methylamines, and/or acetate. Methanogenic archaea are found in diverse environments, such as freshwater sediments, deep-sea volcanoes, swamps, paddy fields, landfills, and the intestinal tracts of ruminants and termites. Methanogens use carbon dioxide as an electron acceptor in the production of methane via a reductive acetyl-CoA pathway and the process known as methanogenesis. During decomposition of biomass in the absence of oxygen, methanogenesis is the final step. Methyl-CoA reductase is the key enzyme and also works as a marker enzyme in methanogenesis. Microbial methanogenesis is the biggest source of methane with an annual production rate of 10^9 tons, e.g., *Methanococcales*, *Methanobacteriales*, *Methanopyrales*, *Methanococcus*, and *Methanosphaera.*

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

8.2 Reductive Citric Acid Cycle or Reductive Tricarboxylic Acid (rTCA) or Arnon-Buchanan Cycle

A new alternative carbon fixation autotrophic pathway is also reported in 1966 in anaerobic green sulfur bacterium *Chlorobium thiosulfatophilum* or *Chlorobium limicola*, called a reductive citric acid cycle or reductive tricarboxylic acid. Further, this cycle is found in anaerobic or microaerobic microbes such as *Aquificae*, *Proteobacteria*, and *Nitrospirae*, in some photosynthetic bacteria *Chlorobium thiosulfatophilum* and *Rhodospirillum rubrum*, and in some microaerobic eubacteria (Hügler et al. 2005; Shiba et al. 1985). Arnon and Buchanan have reported this cycle the very first time, so-called Arnon-Buchanan cycle. This cycle proposed as an alternative cycle for CO_2 assimilation in microbes after the universal occurrence of the Calvin-Benson cycle or Calvin's reductive pentose phosphate cycle. This cycle is reported in both archaeal and bacterial domains. In archaeal domain, it is found in Crenarchaeota – *Thermoproteus neutrophilus*, *Pyrobaculum islandicum*, and *Pyrobaculum aerophilum*. Bacterial domain includes members of microaerophilic Aquificales, *Aquifex aeolicus* and *Aquifex pyrophilus*, also in hyperthermophilic hydrogen-oxidizing bacteria, *Hydrogenobacter thermophilus* and *Hydrogenobacter hydrogenophilus*; sulfur-reducing Crenarchaeota (*Thermoproteus* and *Pyrobaculum*) *Thermocrinis ruber*, *Sulfurihydrogenibium subterraneum*, *Thermovibrio ammonificans*, *Thermovibrio ruber*, *Desulfurobacterium crinifex*, and *Desulfurobacterium thermolithotrophum*; *Desulfobacterales* (delta proteobacteria), *Desulfobacter hydrogenophilus*; *Campylobacterales* (epsilon proteobacteria), *Thiomicrospira denitrificans* and *Candidatus Arcobacter sulfidicus*; and Chlorobiales, *Chlorobium limicola* and *Chlorobium tepidum* (now known as *Chlorobaculum tepidum*) (Buchanan and Evans 1969; Fuchs et al. 1980; Beh et al. 1993; Hügler et al. 2005; Berg 2011).

The reductive citric acid cycle runs in the reverse direction of the citric acid cycle (Krebs cycle), works in reductive method, and produces acetyl-CoA from two molecules of CO_2. This cycle includes a series of chemical reactions for the synthesis of one molecule of acetyl-CoA from two molecules of CO_2 and water. During reverse TCA cycle bacteria, use hydrogen, sulfide, or thiosulfate for electron donors. The reductive citric acid cycle and oxidative tricarboxylic acid cycle have common enzymes such as ATP citrate lyase, 2-oxoglutarate:ferredoxin oxidoreductase, and pyruvate-ferredoxin oxidoreductase. In the rTCA cycle, three enzymes are crucial which allow the cycle to run in reverse process like ATP citrate lyase (citrate cleave into acetyl-CoA and oxaloacetate with the help of ATP molecule), 2-oxoglutarate: ferredoxin oxidoreductase (formation of 2-oxoglutarate due to carboxylation of succinyl-CoA), and fumarate reductase (fumarate to succinate). The rTCA cycle is completed in a reductive way due to modification of several irreversible steps of oxidative TCA cycle, such as the following: Succinate dehydrogenase is replaced by fumarate reductase, NAD + -dependent 2-oxoglutarate dehydrogenase is replaced by ferredoxin-dependent2-oxoglutarate synthase (2-oxoglutarate,ferredoxin oxidoreductase), and citrate synthase is replaced by the ATP citrate lyase. These enzymes are crucial for the accomplishment of reverse TCA or reductive carboxylation process.

The reverse TCA consist of the following steps: The first step is the cleavage reaction of citrate to acetyl-CoA and oxaloacetate by the action of enzyme ATP-citrate lyase ATP molecules hydrolyzed to ADP and Pi. In the case of *Hydrogenobacter thermophilus* bacteria cleavage of citrate is catalyzed by three enzymes ATP-citrate lyase, citryl-CoA lyase (CCL), and citryl-CoA synthase. ATP-citrate lyase synthesized oxaloacetate, whereas citryl-CoA first form citryl-CoA then convert into acetyl-CoA by using catalyst citryl-CoA synthase (CCS). In the next step oxaloacetate is converted to malate with the help of catalyst malate dehydrogenase and NADH/H+ and produced NAD+. Then malate is converted to fumarate and reaction catalyzed by fumarate hydratase, and H_2O molecule is produced in this step. In the next step, fumarate is converted to succinate via a fumarate-reductase (FRD) catalyst, and NADH (electron donor) is converted to NAD in this step.

In the next reaction, ATP dependent succinyl-CoA synthetase used to convert succinate to succinyl-CoA and ATP is hydrolysed to ADP+Pi. Succinyl CoA is now reductively carboxylated and synthesis 2-oxoglutarate with the help of 2-oxoglutrate. In the seventh step, 2-oxoglutrate is reductively carboxylated to isocitrate by isocitrate dehydrogenase (IDH) and utilized NADPH and CO_2 molecules. In the case of *Hydrogenobacter thermophilus*, this step is completed by two different enzymes such as 2-oxoglutrate carboxylase or oxalosuccinate synthetase and oxalosuccinate reductase (OSR). In this step 2-oxoglutarate first converted into oxalosuccinate by using catalyst 2-oxoglutrate carboxylase or oxalosuccinate synthetase and HCO_3, then oxalosuccinate reduced to isocitrate by using oxalosuccinate reductase (OSR). In the last step of the cycle, isocitrate converted into citrate by the catalyst aconitase. Again the catalyst, ATP citrate lyase, is used in the cycle to cleave citrate to oxaloacetate and acetyl-CoA (ATP is hydrolyzed to ADP and Pi). This acetyl-CoA converted into pyruvate by pyruvate-ferredoxin oxidoreductase (POR) (Fig. 5). Hence, in one complete cycle of the reductive carboxylic acid, there is the utilization of four molecules of CO_2 and formation of one oxaloacetate as a final product (Fuchs 2011).

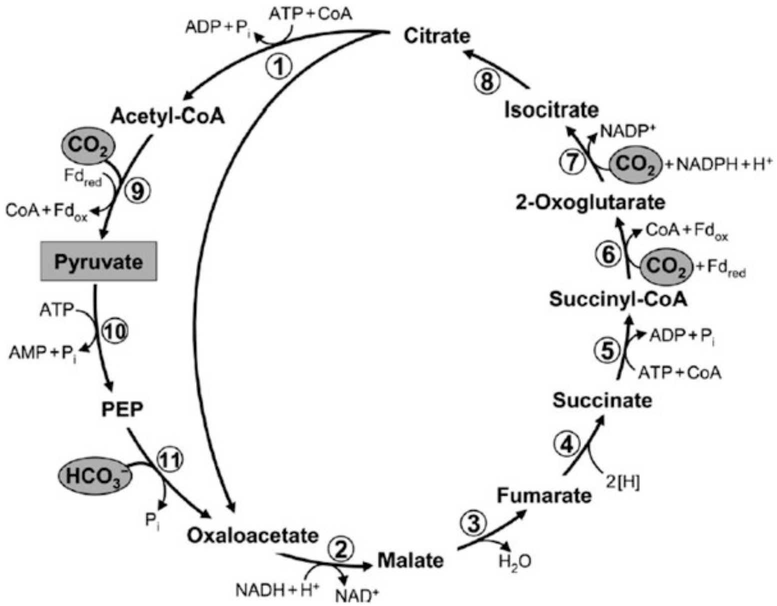

Fig. 5 The reductive citric acid (Arnon-Buchanan) cycle as it functions in green sulfur bacteria. The pathway of acetyl-CoA assimilation to pyruvate, phosphoenolpyruvate (PEP), and oxaloacetate is shown as well. For deviations from this variant of the cycle, see the text. Enzymes: 1, ATP-citrate lyase; 2, malate dehydrogenase; 3, fumarate hydratase; 4, fumarate reductase (natural electron donor is not known); 5, succinyl-CoA synthetase; 6, ferredoxin (Fd)-dependent 2-oxoglutarate synthase; 7, isocitrate dehydrogenase; 8, aconitate hydratase; 9, Fd-dependent pyruvate synthase; 10, PEP synthase; 11, PEP carboxylase. (Adopted from Fuchs 2011)

8.3 Dicarboxylate/4-Hydroxybutyrate Cycle (DC/HB)

Dicarboxylate/4-hydroxybutyrate cycle is another important alternative cycle in various anaerobic or microaerobic autotrophic microbes like *Thermoproteus neutrophilus* (*Thermoproteales*), *Ignicoccus hospitalis (Desulfurococcales)*, and *Metallosphaera sedula (Sulfolobales)*, *Ignicoccus hospitalis (Desulfurococcales)*, and *Pyrolobus fumarii* (*Desulfurococcales*). This unique cycle well explained by Huber et al. 2008 in the hyperthermophilic Archaeum *Ignicoccus hospitalis* (Huber et al. 2008; Erb 2011).

8.3.1 The Cycle Can Be Divided Into Two Parts

The first part of the cycle consists of the utilization of one CO_2 and one bicarbonate by acetyl-CoA and transformed to succinyl-CoA by C_4 dicarboxylic acids. This part uses an oxygen-sensitive enzyme pyruvate synthase and ferredoxin used as an electron donor. As pyruvate synthase lose its activity in presence of oxygen, therefore these reactions of the pathway takes place restrictedly in anaerobes or microaerobes. This part of the cycle start by two enzymes pyruvate synthase and ferredoxin (FD), which form pyruvate due to reductive carboxylation of acetyl-CoA. Further, pyruvate is converted to phosphoenolpyruvate (PEP) and use one ATP molecule and one water molecule. PEP now carboxylated and converted into oxaloacetate via PEP carboxylase enzyme one HCO^{3-} molecule is used in the step. The oxaloacetate undergo reduction and use NADH as electron donor to form (s)-malate with the help of malate dehydrogenase enzyme. (s)-Malate immediately converted into fumarate and release one molecule of water via fumarate hydratase. Fumarate undergo reduction and form succinate via fumarate reductase enzyme. In the next step succinate form succinyl-CoA and utilize one ATP + CoASH molecule. In oxaloacetate reduction consists an incomplete reductive citric acid cycle, which stops at succinyl-CoA; it is not complete as originally thought (Huber et al. 2008).

In the second part of the pathway, succinyl-CoA convert into two molecules of acetyl-CoA via 4-hydroxybutyrate. This part of the cycle is common in both dicarboxylate/4-hydroxybutyrate cycle and 3-hydroxypropionate/4-hydroxybutyrate cycle. In this part, succinyl-CoA is reduced in two steps to 4-hydroxybutyrate. In first step, succinyl-CoA is further reduced and converted in succinic semialdehyde by the catalyst succinyl-CoA reductase and release CoASH coenzyme. Succinic semialdehyde further reduced into 4-hydroxybutyrate with the help of enzyme succinic semialdehyde reductase; NADPH work as an electron donor in this reaction. In the next step of the cycle, 4-hydroxybutyrate utilized the CoASH and one ATP molecule and transformed into 4-hydroxybutyryl-CoA via 4-hydroxybutyrate-CoA ligase. 4-Hydroxybutyryl-CoA further converted into crotonyl-CoA via 4-hydroxybutyryl-CoA dehydratase and released one water molecule. 4-Hydroxybutyryl-CoA dehydratase is one of the key enzymes of the cycle. 4-Hydroxybutyryl-CoA dehydratase is a FAD-containing enzyme and with [4Fe-4S] cluster that catalyzes the elimination of water from 4-hydroxybutyry-CoA by a ketyl radical mechanism. The crotonyl-CoA molecule undergo β-oxidation and form two molecules of acetyl-CoA via three-step reaction. First, crotonyl-CoA transform into (s)-3-hydroxybutyryl-CoA by using one water molecule and crotonyl-CoA hydratase catalyst, the second step (s)-3-hydroxybutyryl-CoA converted into acetoacetyl-CoA with the help of (s)-3-hydroxybutyryl-CoA dehydrogenase and NAD, and in the third step, final product acetyl-CoA produced from acetoacetyl-CoA via catalyst acetoacetyl-CoA β-ketothiolase. Further, crotonyl-CoA is converted into two molecules of acetyl-CoA via β-oxidation reactions. One acetyl-CoA utilized in biosynthesis mechanism and the second one serves as a CO_2 acceptor for the next round of the cycle (Huber et al. 2008; Erb 2011) (Fig. 6).

8.4 3-Hydroxypropionate/4-Hydroxybutyrate Cycle (HP/HB)

The next and crucial CO_2 assimilation cycle present in aerobic autotrophs is a 3-hydroxypropionate/4-hydroxybutyrate cycle. This pathway majorly observed and studied in the member of Sulfolobales like *Sulfolobus metallicus*, Crenarchaeota, *Archaebacteria brierleyi*, and also in obligate anaerobe *Stygiolobusa zoricus* (Fig. 6 Section b). The first time this pathway discovered in archaea

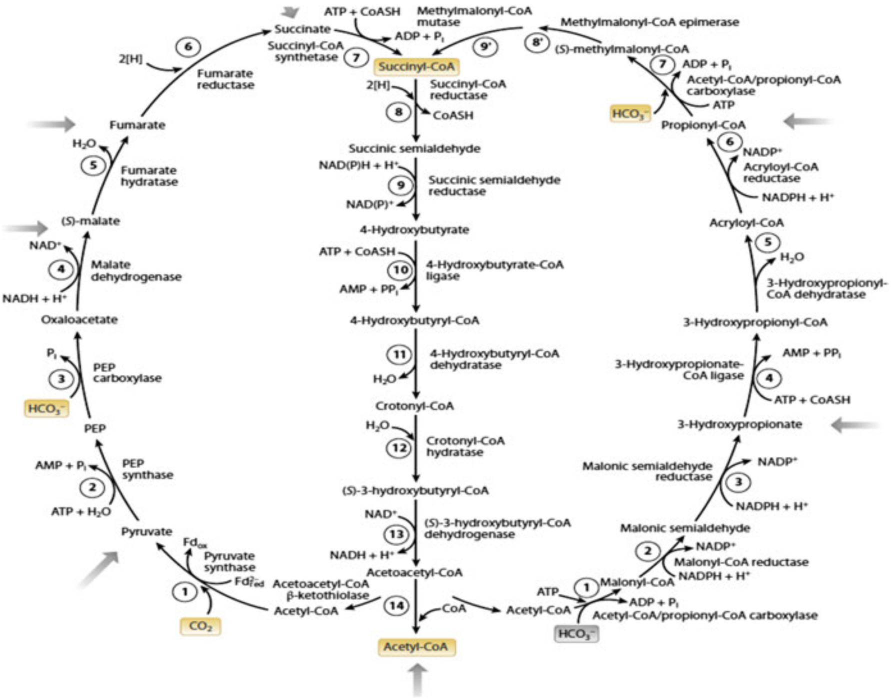

Fig. 6 The 4-hydroxybutyrate cycles of autotrophic CO2 fixation (A) The dicarboxylate/4-hydroxybutyrate cycle functioning in Desulfurococcales and Thermoproteales, and (B) the 3-hydroxypropionate/4-hydroxybutyrate cycle functioning in Sulfolobales. Note that succinyl-CoA reductase in Thermoproteales and Sulfolobales uses NADPH and probably reduced ferredoxin in Desulfurococcales. Enzymes: (1) pyruvate synthase; (2) pyruvate-water dikinase; (3) PEP carboxylase; (4) malate dehydrogenase; (5) fumarate hydratase; (6) fumarate reductase (natural electron acceptor is not known); (7) succinyl-CoA synthetase; (8) acetyl-CoA/propionyl-CoA carboxylase; (9) malonyl-CoA reductase; (10) malonic semialdehyde reductase; (11) 3-hydroxypropionate-CoA ligase; (12) 3-hydroxypropionyl-CoA dehydratase; (13) acryloyl-CoA reductase; (14) methylmalonyl-CoA epimerase; (15) methylmalonyl-CoA mutase; (16) succinyl-CoA reductase; (17) succinic semialdehyde reductase; (18) 4-hydroxybutyrate-CoA ligase; (19) 4-hydroxybutyryl-CoA dehydratase; (20) crotonyl-CoA hydratase; (21) (S)-3-hydroxybutyryl-CoA dehydrogenase (NAD+); (22) acetoacetyl-CoA β -ketothiolase. Fd, ferredoxin. The gray arrows show the entry of various organic substrates. (Adopted from Fuchs 2011)

Metallosphaera sedula and the phototrophic filamentous green non-sulfur bacterium *Chloroflexus aurantiacus.* The 3-hydroxypropionate/4-hydroxybutyrate (3HP/4HB) cycle is crucial for biogeochemical CO_2 fixations due to many reasons like it can work in high temperature, the pathway consists high potential for rapid kinetics and also can work in aerobic or anaerobic autotrophs unlike the dicarboxylate/4-hydroxybutyrate cycle and reductive acetyl-CoA pathways. This cycle completed by five important thermostable enzymes malonyl-CoA/succinyl-CoA reductase, 3-hydroxypropionyl-CoA synthetase, 3 hydroxypropionyl-CoA dehydratase, acryloyl-CoA reductase, and succinic semialdehyde reductase. Acetyl-CoA/

propionyl-CoA carboxylase (ACC) and hydroxybutyryl-CoA synthetase (HBCS) is the prime enzymes to regulate the cycle. In the HP cycle, two molecules of bicarbonate utilized and one molecule of acetyl-CoA synthesized as a final product. For the better understanding 3-hydroxypropionate cycle (HP) can be divided into three sub-pathways.

In the first sub-pathway-acetyl-CoA is carboxylated by acetyl-CoA/propionyl-CoA carboxylase (ACC) and subsequently reduced to the stable intermediate 3-hydroxypropionate(3HP). Biotin-dependent acetyl-CoA/propionyl-CoA carboxylase are bifunctional enzyme.

This reaction is completed in three steps: in the first step firstly, carboxylation takes place and acetyl coenzyme A (acetyl-CoA) is converted into malonyl-CoA by using ATP-dependent biotin-containing acetyl-CoA carboxylase. In the second step-Malonyl-CoA converted into malonic semialdehyde by using malonyl-CoA reductase and NADPH as the electron donor. In third step-Malonic semialdehyde undergo in reduction and converted into 3-hydroxypropionate by using malonic semialdehyde reductase and NADPH work as the electron donor.

In the second sub-pathway, 3-hydroxypropionate use the coenzyme A (CoA) molecule and reduced to propionyl-CoA and further carboxylated by acryloyl-CoA reductase (ACC) and converted into succinyl-CoA. Next, the second stable intermediate compound 4-hydroxybutyrate (4HB) synthesized from the reduction of succinyl-CoA. This second sub-pathway is completed via multiple steps (Fig. 6, reactions 4–12). 3-Hydroxypropionate converted into 3-hydroxypropionyl-CoA via 3-hydroxypropionate-CoA ligase enzyme, CaASH coenzyme, and ATP molecule. Then 3-hydroxypropionyl-CoA converted into acryloyl-CoA with the help of 3-hydroxypropionyl-CoA dehydratase and one water molecule release. Propionyl-CoA synthesized from Acryloyl-CoA due to reduction reaction in the presence of Acryloyl-CoA reductase catalyst and NADPH work as an electron donor. Propionyl-CoA utilizes the HCO^{3-} molecule and ATP for carboxylation in the presence of Acetyl-CoA/propionyl-CoA carboxylase catalyst and form (S)-methylmalonyl-CoA which immediately converted into succinyl-CoA via methylmalonyl-CoA epimerase. Succinyl-CoA via further converted into succinic semialdehyde and then 4-hydroxybutyrate via succinyl-CoA reductase and succinic semialdehyde reductase, respectively. In these steps, CoA thioester (CoASH) release and NADPH are utilized.

In the third sub-pathway, starting molecule acetyl-CoA of the HP pathway is regenerated from 4-hydroxybutyrate by using CoA. This complete sub-pathway are completed in five steps: −4-Hydroxybutyrate converted into 4-hydroxybutyryl-CoA via 4-hydroxybutyrate-CoA ligase and ATP + CoASH molecule. 4-Hydroxybutyryl-CoA released the water molecule and converted into Crotonyl-CoA by using 4-hydroxybutyryl-CoA dehydratase as a catalyst. Crotonyl-CoA further converted into (S)-3-hydroxybutyryl-CoA and acetoacetyl-CoA by using crotonyl-CoA hydratase and (S)-3-hydroxybutyryl-CoA dehydrogenase, respectively. Now acetyl-CoA regenerated from acetoacetyl-CoA. This third sub-pathway is common in both the cycle dicarboxylate/4-hydroxybutyrate cycle (DH) and the 3-hydroxypropionate cycle (HP). The enzymes of the HP pathway are oxygen tolerant unlike to DH pathway so the cycle can function in oxic conditions (Fig. 6) (Berg et al. 2007; Fuchs 2011; Berg 2011).

8.5 3-Hydroxypropionate Bicycle

The 3-hydroxypropionate pathway or 3-hydroxypropionate bicycle or Fuchs-Holo pathway, a carbon assimilation pathway described in the thermophilic green non-sulfur bacteria *Chloroflexus aurantiacus.* This pathway was first suggested by Holo (1989) and designed the first draft of the cycle. The further main frame of the cycle explained by Holo (1989); Beh et al. (1993); Herter et al. (2002); Zarzycki et al. (2009); and Fuchs (2011). In the 3-Hydroxypropionate Bi-Cycle, *Chloroflexus aurantiacus* is used as a model system and in the mechanism two molecules of bicarbonate is utilised and one molecule of glyoxylate is synthesised. 3-hydroxypropionate bicycle can be divided into two sub-cycles:

8.5.1 In the First Sub-cycle

First CO_2 converted into bicarbonate and then two molecules of bicarbonate utilized per turn and one molecule of glyoxylate synthesized. Glyoxylate is not a central precursor molecule for the metabolisms, so it converted into further essential organic molecule for the cell by the second sub-cycle. The first sub-cycle accomplished by multiple steps (Fig. 7). In the first reaction of the pathway, acetyl-CoA is carboxylated to malonyl-CoA by acetyl-CoA carboxylase; here utilization of two molecules of HCO^{3-} and 2 molecule of ATP takes place. In the next reaction reduction of malonyl-CoA takes place by bifunctional malonyl-CoA reductase catalyst and forms 3-hydroxypropionate as an intermediate, in this step 2CoA released and $4NADPH_2$ used. 3-Hydroxypropionate binds to CoA and uses two molecules of $NADPH_2$ and two molecules of ATP and then immediately converted into propionyl-CoA by trifunctional propionyl-CoA synthase catalyst.

In the next step, propionyl-CoA is carboxylated to (s)-methylmalonyl-CoA by using HCO^{3-}, ATP, and propionyl-CoA carboxylase enzyme. (s)-Methylmalonyl-CoA followed the isomerization and converted into succinyl-CoA via two steps reaction which is catalyzed by methylmalonyl-CoA epimerase and methylmalonyl-CoA mutase. Succinyl-CoA release the CoA via transferase succinyl-CoA-(S)-malate-CoA transferase and form fumarate and then (S) malate via succinate dehydrogenase and fumarate hydratase enzymes, respectively. (S)-Malate bind with CoA and form (S)-malyl-CoA (second intermediate molecule). In the last step of the first sub-cycle, (S)-malyl-CoA is cleaved into acetyl-CoA and glyoxylate via malyl-CoA lyase. The released glyoxylate is the first carbon fixation product of the cycle. Acetyl-CoA takes part into another round of first sub-cycle, whereas glyoxylate now used by the second sub-cycle of the Fuchs-Holo pathway for the synthesis of pyruvate and acetyl-CoA. Therefore, the cycling term is 3-hydroxypropionate bicycle. The second sub-cycle: It is a regeneration cycle where precursors molecule (acetyl-CoA) of the cycle resynthesized. Synthesized glyoxylate and intermediate propionyl-CoA molecule are converted to pyruvate and

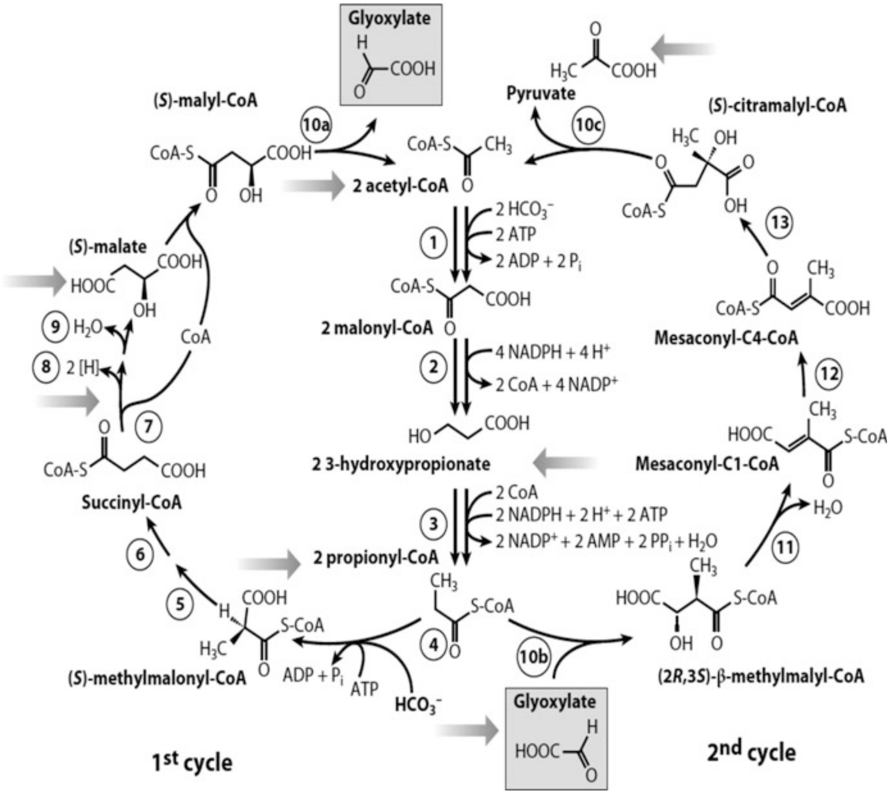

Fig. 7 3-Hydroxypropionate bicycle. The gray arrows show the entry of various organic substrates. Enzymes as studied in *Chloroflexus aurantiacus*. Reaction 1: Acetyl-CoA carboxylase (ADP forming). Reaction 2: Malonyl-CoA reductase (NADPH). Reaction 3: Propionyl-CoA synthase (AMP forming, NADPH). Reaction 4: Propionyl-CoA carboxylase (ADP forming). Reaction 5: Methylmalonyl-CoA epimerase. Reaction 6: Methylmalonyl-CoA mutase. Reaction 7: Succinyl-CoA:(S)- malate-CoA transferase. Reaction 8: Succinate dehydrogenase (quinone). Reaction 9: Fumarate hydratase. Reaction 10a: (S)-malyl-CoA lyase. Reaction 10b: β-Methylmalyl-CoA lyase. Reaction 11: Mesaconyl-C1-CoA hydratase (β-methylmalyl-CoA dehydratase). Reaction 12: Mesaconyl-CoA C1-C4 CoA transferase. Reaction 13: Mesaconyl-C4-CoA hydratase. Reaction 10c: (S)-citramalyl-CoA lyase. (Adopted from Fuchs 2011)

acetyl-CoA. This pathway depends on several enzymes which can work under aerobic and anaerobic conditions (Zarzycki et al. 2009). In the second sub-cycle, glyoxylate assimilation starts and regeneration of acetyl-CoA occurs. In the first step propionyl-CoA (an intermediate of the first cycle) bind to the glyoxylate and form β-methylmalyl-CoA (C1) via methylmalyl-CoA lyase, which is immediately converted into mesaconyl-CoA (C4) via mesaconyl-CoA C1-C4 CoA transferase. The mesaconyl-CoA converted into unstable (S)-citramalyl-CoA with the help of mesaconyl-C4-CoA hydratase. The unstable (S)-citramalyl-CoA is immediately cleaved into acetyl-CoA and pyruvate by a trifunctional lyase. In the

3-hydroxypropionate bicycle 19 steps completed via only 13 enzymes and pyruvate form for the cell carbon from 3 molecules of bicarbonate (Zarzycki et al. 2009; Zarzycki and Fuchs 2011; Shih et al. 2017) (Fig. 7).

9 Impact of Global Carbon Cycle on Mitigation of Climate Change Through Microbial Carbon Flux

Balancing of carbon concentration between the biosphere and atmosphere is very crucial for global climate variations. Sequestration of carbon and fluxes in various sinks is essential for mitigation of climate change. The most crucial strategies to deal with climate change are balancing the concentration of carbon dioxide (CO_2) in the atmosphere. During carbon sequestration, CO_2 is absorbed by the vegetation and stored in the soil. Carbon source is not only impactful to maintain CO_2 concentration in the atmosphere but also affects the soil health, soil organisms habitat, and waste recycling (Lal 2004; Fung et al. 2005; Schimel et al. 2015). The increasing concentration of CO_2 and other greenhouse gases like carbon dioxide, methane, nitrous oxide, and ozone in the atmosphere adversely affects the Earth climate. All these factors play a crucial role in climate variations and regulate the temperature of our atmosphere. Variation in atmospheric climate and temperature also adversely affects the soil productivity, plant reproduction, annual rainfall, function of ecosystems, and global economy. Carbon dioxide is not the only greenhouse gas which is responsible for global warming; other greenhouse gases (GHGs) like CH_4 also play a vital role. Sun's heat significantly trapped by atmospheric methane and increase the global temperature. There are various resources like agriculture, biomass burning, energy production, and industries gases, by which CH_4 is released in the atmosphere like agriculture, and fluctuations of CH_4 emissions strongly affect climate warming. Therefore, mitigation of climate change can be possible by balancing the greenhouse gases below the carbon budget and also increase the microbial, marine, and terrestrial vegetation carbon sequestration processes (Raupach et al. 2008; Meena and Lal 2018; Pan et al. 2011; Sellers et al. 2018).

The recent studies reviles that approximately 1.2 × 1030 microbial cells are present on Earth, out of which deep oceanic subsurface consists around 4 × 1029, upper oceanic sediment consists around 5 × 1028, deep continental subsurface consists 3 × 1029 whereas soil represents 3 × 1029 (Flemming and Wuertz 2019), such complex microbial diversity and their metabolic pathways greatly affect the ecosystems health through the energy flux and cycling of the nutrient components. All the organic and inorganic compounds used by the microbes for the carbon fixation play a vital role in carbon flux between the various ecosystems, which have a direct impact on the climate of our atmosphere (Weiman 2015). Soil microbiome has a strong relationship with global climate changes, carbon cycling, and other biogeochemical cycles (Dubey et al. 2019). Microbes are highly diverse and can survive in under various kind of stresses due to its easy gene manipulation. Microbes are complex and follow multiple pathways for the assimilation of carbon; therefore, climate conditions are directly or indirectly affected by microbial metabolisms. Microbes consume the greenhouse gases (carbon dioxide, methane, and nitrous oxide) which is a link with climate change. Exchange of carbon molecules between soil and atmosphere is the reflection of respiration, decomposition, and carbon fixing metabolic pathways. Microbial community plays a crucial role in the biogeochemical cycle, affecting the atmospheric climate directly. Atmospheric carbon dioxide is fixed by the photosynthetic microbes and returns to the atmosphere by the decomposition of organic matter by the heterotrophic decomposers. The total carbon flux and balance between these two processes is crucial to maintain atmospheric climate. Hence, the vast knowledge of microbial diversity and their several metabolisms enhance our understanding of carbon cycle and complex interaction between all the carbon reservoirs and its significant impact on climate change.

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Role of Soil Microbes and Their Cell Components in Carbon Stabilization

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Abstract

Fixation of carbon dioxide (CO_2) for the production of organic compounds is carried out globally by microbes. These microbes provide food for the survival of heterotrophs in terms of organic C through CO_2 fixation. The most familiar pathway of carbon (C) fixation is Calvin–Benson–Bassham cycle. This pathway is adopted by plants, microbes, and algae for inorganic C fixation in natural environment. However, there are a number of other pathways as well that are specifically adopted by microbes for C fixation. By adopting these pathways, microbes follow diversified chemical and biochemical strategies. This chapter is providing basic knowledge about the fixation of CO_2 by microbes, mechanism involved in the fixation of CO_2, and the enzymes which regulate these mechanisms. Five major pathways, i.e., Calvin-Benson-Bassham cycle, reductive tricarboxylic acid cycle, 3-hydroxypropionic acid (3-HP) cycle, reductive acetyl-CoA (rACo) pathway, and carboxylases, are discussed in this chapter. Four C-fixing pathway enzymes have been described in the chapter. In the near future, it is expected that new pathways will also be established due to number and diversity of microorganisms.

Keywords

Carbon · Microbes · PGPR · Enzymes · Fixation

Abbreviations

3-HP	3-Hydroxypropionic acid
3-HP	3-Hydroxypropionic acid
3-PGA	3 Phosphoglyceric acid
acetyl-CoA	Acetyl-coenzyme A
AMF	Arbuscular mycorrhiza fungi
ATP	Adenosine triphosphate
HCO3−	Bicarbonates ion
CBB	Calvin-Benson-Bassham cycle
C	Carbon
CO_2	Carbon dioxide
CCL	Citryl-CoA lyase
GT	Giga ton
G3P	Glyceraldehyde 3-phosphate
kDa	Kilodalton

NADPH	Nicotinamide adenine dinucleotide phosphate
Pi	Phosphate
FADH2	Reduced flavin adenine dinucleotide
rACo	Reductive acetyl-CoA
rTCA	Reductive tricarboxylic acid cycle
RuBisCO	Ribulose-1,5-bisphosphate carboxylase/oxygenase

1 Introduction

Text of introduction presence of carbon dioxide (CO_2) in atmosphere beyond the safe limit (350 ppm) has declared global warming the most concerned issue of the environment (Agarwal et al. 2017). In soil formation, pedogenic processes fix soil inorganic carbon (C) in the form of bicarbonates (Sollins et al. 1996). However, burning of fuels by industries and automobiles releases a significant amount of CO_2 in the atmosphere. This CO_2 is a major part of bioprocess named autotrophy. Forest ecosystem are being deeply and widely investigated all over the world for their significant role in CO_2 fixation. In these ecosystems, C storage and cycling serve as general indicators to find out the CO_2 fixation potential. Selection and screening of most efficient forest trees species is an area of high interest nowadays (Zhou et al. 2011). Forests are reported to be the most efficient system in this regard. Mostly forest ecosystems have C fixation ability up to 14.80 t/ha/a. After bamboo ecosystem, slash pine forests are the most efficient CO_2 fixers followed by the broadleaved forest, rounding trees, cypress forest, mass on pine, and Chinese fir, open and shrub, respectively (Yuan et al. 2004). Oceanic CO_2 fixation takes place through various routes. Photosynthesis takes place in oceans. Phytoplankton photosynthesis is very important in this regard (Rivkin and Legendre 2001) that have capacity to fix about 45×10^{15} g carbon per year (Falkowski et al. 2000). As we are always in close contact with the land plants, different and interesting aspects of ocean plants are ignored. But sometimes, oceanic plant life has a very big impact. Photosynthetic organisms of ocean have an important role in CO_2 fixation and contribute a lot toward biogeochemical cycles. Phytoplankton are reported to be effective players in this context. They are single-celled oxygenic organisms. Plankton is a Greek word with meanings of to drift. Phytoplankton biomass amounts 1–2% of the plant C. In spite of this low percentage, phytoplankton fix about 30 to 50 × 109 metric tons of C per year. It is about 40% of the total global C fixation (Falkowski 1992). On geological canvas, the extent and significance of phytoplankton C fixation in the flux of the biogeochemistry of the planet along with the atmosphere and that of oceans occupy good place (Sarmiento and Siegenthaler 1992).

Since plants play an imperative role in C fixation, microbial C fixation is mostly ignored (Agarwal et al. 2017). World CO_2 fixation potential through autotrophs is estimated to be 380 billion tons per year, but the specific C fixation capacity is reported to be comparatively very low (Field et al. 1998). Bacterial autotrophs are able to use light as well as inorganic chemicals to get energy. However, the pathways which are used by bacterial autotrophs are center of interest in multiple fields of research (Sato and Atomi 2010). If we consider cyanobacteria, they have potential to fix C up to near 1–5 mg/L/h, which is lower than the needs of the industry which is thought to be 1–10 g/L/h (Angermayr et al. 2015). In this chapter, microbial C fixation, their adopted major pathways, and enzymatic reactions are discussed, which could be helpful in improvement of soil health in the future. This chapter will be helpful in understanding the enzymatic reaction involved in C fixation through different microbial pathways.

2 Carbon Dioxide Fixation

Global C economy revolves around the conversion of inorganic CO_2 into organic chemical compounds. CO_2 fixation provides human beings with a source of energy to be consumed in the form of hydrocarbons, alcohols, organic acids, etc. C exists in its higher oxidation state in CO_2 molecules as compared to in fuels and biochemicals. A big energy input is needed to produce biochemicals from inorganic CO_2. So, CO_2 is not commonly used in industries related to the chemical synthesis. Certain autotrophs fix atmospheric CO_2 referred as biological C fixation. The ultimate products of biological C fixation contain longer chain compounds of C, hydrogen, and oxygen which render them more suitable to be used as biofuels and chemicals (Gong et al. 2018).

Atmospheric C is fixed by autotrophic organisms. These autotrophic organisms include photosynthetic plants and photoautotrophic and chemoautotrophic microorganisms (Trumbore 2006). Nonphototrophic CO_2 fixation has also been reported to occur in soils, and most of the resulting products generated are organic compounds in nature. A huge input of energy is needed for CO_2 fixation. Autotrophs naturally utilize light, hydrogen, and/or sulfur as energy inputs. Light being freely available energy input is used by photoautotrophs like plants, algae, and photosynthetic microbes. Photosystems I and II are the main photoreaction complexes, absorbing light of wavelengths ranging between 400 and 700 nm to produce adenosine triphosphate (ATP) and reduced nicotinamide adenine dinucleotide phosphate (NADPH), resultantly providing the required energy for the CO_2 fixation (Meena et al. 2020a; Zhou et al. 2016).

The quantity of C fixed in soil is the largest pool of C on the planet. Total C quantity in terrestrial ecosystems is estimated to be 3170×10^9 t. Of this fixed C, almost 80% rests in soil (Lal 2008). C exists in soil either in organic (1550×10^9 t) or inorganic forms (950×10^9 t). The inorganic form includes elemental C and carbonates, e.g., calcite, dolomite, and gypsum (Lal 2004). The quantity of C in plants and animals is smaller than that in soil (560×10^9 t). It is an important fact that the soil C reserves are near 3.1 times bigger as compared to the C in atmosphere, i.e., 800×10^9 t (Oelkers and Cole 2008; Meena and Lal 2018). On the other hand, ocean C is larger than the soil pool of C, i.e., 38,400 GT. Ocean C is mostly in inorganic forms (Houghton 2007).

3 Soil Microbes-Carbon Dioxide

Phototrophic bacteria with a significant potential of CO_2 fixation are found in all the soil ecosystems (Nakai et al. 2012). The CO_2 fixation rate through autotrophic bacteria has been estimated to be ranging between 0.6 and 4.9 × 10^{15} g carbon per annum (Ge et al. 2013). In rhizosphere, diversity and biomass of microbes are associated with the level of CO_2 in the atmosphere (Paterson et al. 1997). Exudates of plant roots that are composed of 5–40% photosynthetically fixed C attract the soil microbes in rhizosphere (Marschner 1995, 2012; Hinsinger et al. 2006). Fixation of bicarbonates ions (HCO_3^-) and CO_2 (Table 1) by microbes is termed as microbial C fixation. Most of ecosystems are directly associated with organic C which is fixed by autotrophs, i.e., plants and microbes. Furthermore, cyanobacteria, algae, and archaea also play an imperative role in the fixation of C. These autotrophs fix 7 × 10^6 g net CO_2 every year, thus exerting a significant influence in the reduction of global warming (Lacis et al. 2010; Meena et al. 2020b; Berg 2011). Microbial autotrophs utilize fixed C in the synthesis of their cellular components, that's why they are enriched with ^{12}C as compared to $^{13}C/^{12}C$ ratio of inorganic C (Schidlowski 2000).

Autotrophic bacteria have developed six pathways for CO_2 fixation, (i) Calvin-Benson-Bassham cycle, (ii) reductive tricarboxylic acid cycle, (iii) reductive acetyl-CoA pathway, (iv) 3-hydroxypropionate cycle, (v) 3-hydroxypropionate/4-hydroxybutyrate pathway, and (vi) dicarboxylate/4-hydroxybutyrate cycle (Fuchs 2011). The most common pathway found for autotrophic bacteria to fix CO_2 is the Calvin-Benson-Bassham cycle (CBB) (Selesi et al. 2005).

4 Microbial Pathway Involved in Carbon Dioxide Fixation

In an eco-friendly manner, autotrophs fix the atmospheric C by following different pathways (see Sects. 4.1, 4.2, 4.3, 4.4, and 4.5).

4.1 Calvin-Benson-Bassham Cycle

In all over the world, CBB is most common and well-documented pathway for CO_2 fixation found in aerobic or aerotolerant bacteria (Shively et al. 1998; Berg 2011). Almost all the cyanobacteria and some of the bacteria utilize carboxysomes to concentrate CO_2 (Reinhold et al. 1991). Carboxysomes are protein shells filled with the enzyme ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) and a carbonic anhydrase. The carbonic anhydrase produces CO_2 from the bicarbonate that diffuses into the carboxysome. The surrounding shell provides a barrier to CO_2 loss, helping to increase its concentration around RuBisCO (Reinhold et al. 1991). For optimum operation of CBB upper, the temperature limit is ~70–75 °C. The three major steps involved in this cycle are as follows.

Table 1 Different microbes that fix different carbon type

Microbe	Carbon type	References
Synechocystis sp., *Anabaena variabilis*, *Anacystis nidulans*, *Prochlorococcus* sp., *Synechococcus* sp., *Oscillochloris trichoides*, *Ralstonia eutropha*, *Allochromatium vinosum*, *Nitrosococcus oceani*, *Alkalilimnicola ehrlichii*, *Halorhodospira halophila*, *Halothiobacillus neapolitanus*, *Nitrococcus mobilis*, *Methylococcus capsulatus*, *Hydrogenovibrio marinus*, *Thiomicrospira crunogena*, *Rhodospirillum rubrum*, *Acidithiobacillus ferrooxidans*, *Ralstonia eutropha*, *Thiomonas intermedia*, *Cupriavidus metallidurans*, *Thiobacillus denitrificans* sp., *Nitrosomonas europaea*, *Nitrosomonas eutropha*, *Nitrosospira multiformis*, *Burkholderia xenovorans*, *Hydrogenophaga pseudoflava*, *Chlorobium limicola*, *Chlorobium tepidum*, *Ignicoccus hospitalis*, *Thermoproteus neutrophilus*	CO_2	Yang et al. (2002), Campbell and Gary (2004), Badger and Bek (2008), Berberoğlu et al. (2008), Kuznetsov et al. (2011) and Hügler and Sievert (2011)
Thermoproteus neutrophilus, *Pyrobaculum islandicum*, *Magnetotactic coccus*, *Desulfobacterium autotrophicum*, *Methanobacterium thermoautotrophicum*, *Desulfovibrio baarsii*, *Methanosarcina barkeri*, *Clostridium thermoaceticum*, *Methanopyrus*, *Clostridium formicoaceticum*, *Methanococcus*, *Acetobacterium woodii*, and *Methanothermus*, *Metallosphaera sedula*, *Acidianus brierleyi*, *Sulfolobus metallicus*, *Acidianus infernus*, *Acidianus brierleyi*, *Metallosphaera sedula*	HCO_3^-	Williams et al. (2006), Hu and Holden (2006), Berg et al. (2010), Berg (2011), Saini et al. (2011) and Hügler and Sievert (2011)

4.1.1 Carbon Fixation

A large number of prokaryotes rely on CBB cycle for CO_2 fixation. In the cycle, enzyme rubisco catalyze the reaction of carboxylation. Energy-rich molecules, i.e., ATP and NADPH that are produced in photosynthesis, are utilized in Calvin-Benson-Bassham cycle (CBB) as a source of energy (Shively et al. 1998). For synthesis of glyceraldehyde-3-phosphate (G-3-P), CBB requires 9 ATP and 6 NADH to fix 3 molecules of CO_2. In this step, ribulose-1,5-bisphosphate combines with CO_2 that gives 6C compound. This 6C compound is further divided into 3C phosphoglyceric acid (3-PGA) which is catalyzed by enzyme RuBP carboxylase/oxygenase. Thus, one CO_2 gives two molecules of 3-PGA (Fig. 1).

4.1.2 Reduction

The reduction stage of the Calvin cycle, which requires ATP and NADPH, converts 3-PGA (from the fixation stage) into a three-carbon sugar. This process occurs in two major steps:

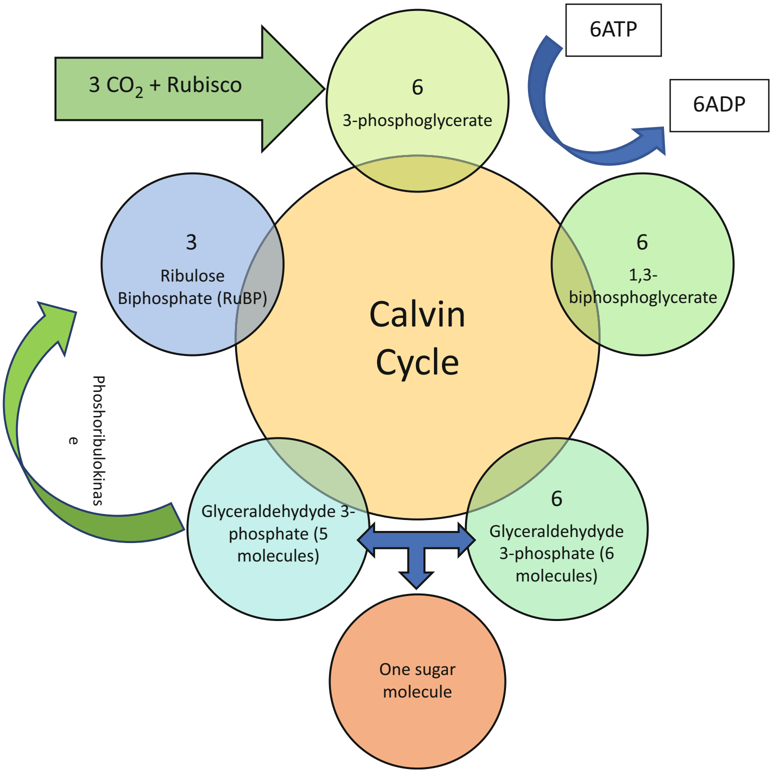


Fig. 1 Carbon fixation in Calvin-Benson-Bassham cycle

Firstly, each molecule of 3-PGA receives a phosphate group from ATP, turning into a doubly phosphorylated molecule called 1,3-bisphosphoglycerate (and leaving behind ADP as a by-product).

Secondly, the 1,3-bisphosphoglycerate molecules are reduced (gain electrons). Each molecule receives two electrons from NADPH and loses one of its phosphate groups, turning into a three-carbon sugar called glyceraldehyde 3-phosphate (G3P). This step produces $NADP^+$ and phosphate (Pi) as by-products.

4.1.3 Regeneration

At this point, only one of the G3P molecules leaves the Calvin cycle and is sent to the cytoplasm to contribute to the formation of other compounds needed by the plant. Because the G3P exported from the chloroplast has three C atoms, it takes three turns of the Calvin cycle to fix enough net C to export one G3P. But each turn makes two G3Ps; thus three turns make six G3Ps. One is exported, while the remaining five G3P molecules remain in the cycle and are used to regenerate RuBP, which enables the system to prepare for more CO_2 to fix (Yuan et al. 2012; Meena et al. 2020). Three more molecules of ATP are used in these regeneration reactions.

4.2 Reductive Tricarboxylic Acid Cycle (rTCA)

Evans et al. (1966) first proposed this reductive tricarboxylic acid (rTCA) cycle. The cycle supported the discovery of ferredoxin-dependent pyruvate and 2-oxoglutarate synthase. However, later on existence of ATP citrate-lyase was also established. This allow a reverse flux of well-established TCA (Sintsov et al. 1980). During this cycle two molecules of CO_2 are fixed which produced single acetyl-CoA molecule. This acetyl-CoA is converted into pyruvate as phosphoenolpyruvate that are involved in anaplerotic reactions. The anaplerotic reactions is catalyzed by phosphoenolpyruvate carboxylase and pyruvate synthase. For energy ATP, NADPH, and FADH2 are utilized that take CO_2 from environment and make it part of metabolism. It works under such environment that have plenty of CO_2, reducing agents and very little organic C. Over Calvin cycle, rTCA consumed less energy. Mostly anaerobic or microaerophilic bacteria and archaea adopt this pathway. The photoautotrophic growth of green sulfur bacteria, i.e., *Chlorobaculum tepidum* and *Chlorobium limicola*, fixes CO_2 by rTCA (Sintsov et al. 1980; Tang and Blankenship 2010). Members of ε-proteobacteria also demonstrate the abundance of rTCA genes (Hügler et al. 2005). The key enzymes of the cycle are oxoglutarate synthase (2-oxoglutarate: ferredoxin oxidoreductase) and the citrate breaking enzymes, viz., ATP citrate lyase or citryl-CoA lyase (CCL), whereas other enzymes of the cycle are common for both oxidative and reductive TCAs (Fig. 2).

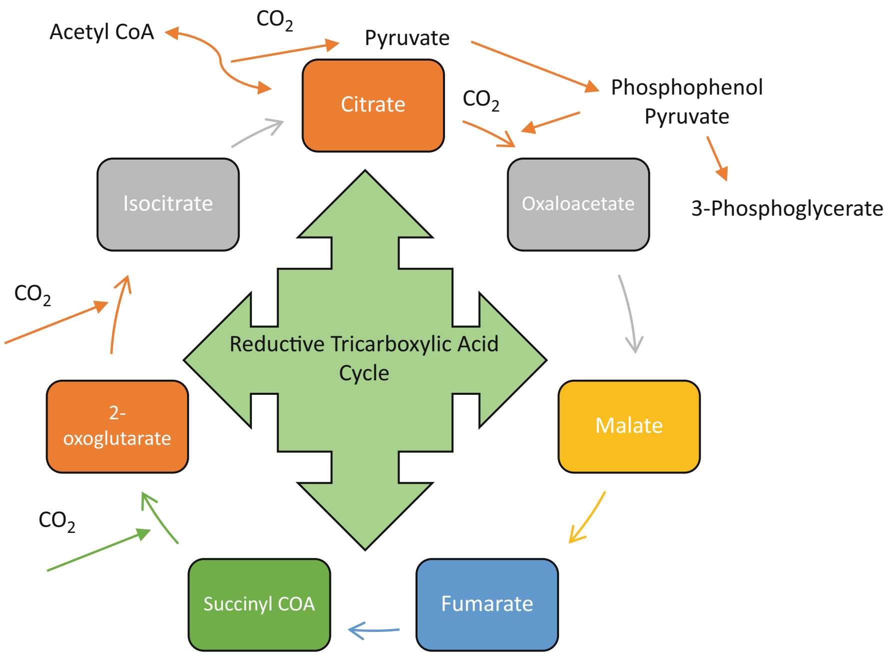


Fig. 2 Reductive tricarboxylic acid cycle representing fixation of two molecules of CO_2 and the key enzymes and CO_2-fixing enzymes of the cycle

4.3 3-Hydroxypropionic Acid (3-HP) Cycle

3-Hydroxypropionic acid (3-HP) is a nonchiral carboxylic acid that contains a hydroxyl group on its third C atom and has a high potential as a platform compound to produce many other chemicals, such as 1,3-propanediol (Kim et al. 2014). In the year 2010, 3-HP was regarded as one of the top value-added chemicals produced from biomass by the US Department of Energy (Bozell and Petersen 2010). It is one of the oldest pathways for the fixation of CO_2 which was investigated in *Chloroflexus aurantiacus* bacterium under aerobic facultative phototrophic conditions (Holo 1989). For the manufacturing of glyoxylate, this pathway utilizes acetyl and propionyl-CoA carboxylases that regenerates malonyl-CoA and (S)-methylmalonyl-CoA, respectively. It also fixes two molecules of CO_2. Further, malonyl-CoA, in a series of reactions, further splits into acetyl-CoA and glyoxylate. Glyoxylate is incorporated into beta-methylmalyl-CoA which then splits again through a series of reactions to release pyruvate as well as acetate, which is used to replenish the cycle (Berg et al. 2010).

4.4 Reductive Acetyl-CoA (rACo) Pathway

This pathway is a non-cyclic pathway for the fixation of C dioxide. Mostly, anaerobic, methanogenic, and acetogenic bacteria regulate fixation of C via reductive acetyl-CoA pathway (Hügler and Sievert 2011). When CO_2 enters into bacteria and Archaea, rACo reduces it into carbonyl and methyl branches. Initially, CO_2 is reduced to C monoxide and formic acid or directly into a formyl group (Fig. 3). After that the formyl group is reduced to a methyl group and then combined with the carbon monoxide (CO) and coenzyme A to produce acetyl-CoA. Two specific enzymes participate on the carbon monoxide side of the pathway: CO dehydrogenase and acetyl-CoA synthase (Ragsdale 2006; Lindahl 2009). During this type of C fixation, bacteria produce acetates. However, in the archaea it is converted into methane (Christopher et al. 2016).

4.5 Carboxylases

This pathway shares 98% of C fixation via biological hosts (Table 2). It plays an imperative role for marinating the level of CO_2 in the atmosphere (Thauer et al. 2008). There are five major steps which regulate carboxylases. These steps are as follows;

1. Autotrophic carboxylases
2. Assimilatory carboxylases
3. Anaplerotic carboxylases
4. Biosynthetic carboxylases
5. Redox-balancing carboxylases

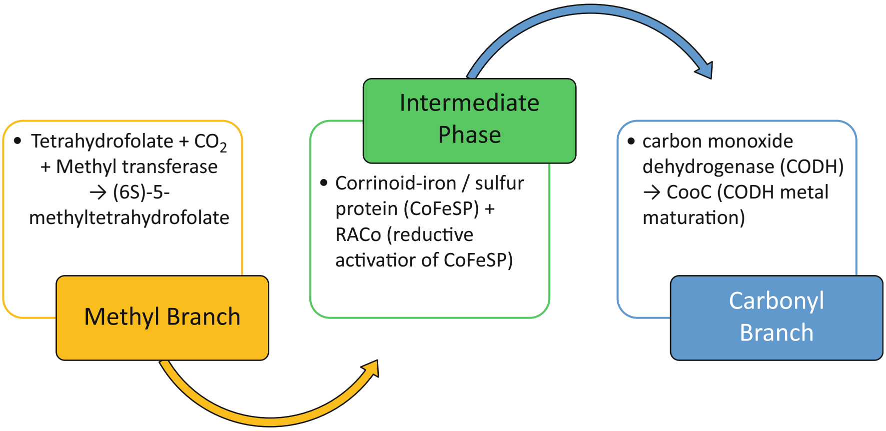


Fig. 3 Reductive acetyl-CoA (rACo) pathway

Table 2 Different microbes and their pathway for carbon dioxide fixation

Pathway	Microbe	References
Calvin-Benson-Bassham cycle	**Cyanobacteria** *Synechococcus*, *Anacystis*, *Anabaena* **Purple nonsulfur bacteria** *Rhodobacter*, *Rhodospirillum*, *Rhodopseudomonas* **Purple sulfur bacteria** *Chromatium* **Some hydrogen-oxidizers** *Ralstonia*, *Hydrogenovibrio* **Some sulfur-oxidizers (chemoautotrophs)** *Thiobacillus* **Nitrite-oxidizers** *Nitrobacter* **Ammonia-oxidizers** *Nitrosomonas*, *Nitrosococcus*, *Nitrosospira*	Tichi and Tabita (2000), Atomi (2002) and Sato and Atomi (2010)
Acetyl-CoA pathway	**Acetogens** *Clostridium*, *Acetobacterium* **Some sulfate-reducers** *Desulfobacterium*, *Desulfovibrio* **Methanogens** *Methanobacterium*, *Methanosphaera*, *Methanothermobacter*, *Methanothermus*, *Methanocaldococcus*, *Methanococcus*, *Methanospirillum*, *Methanosarcina*, and *Methanopyrus* **Some hydrogen oxidizers** *Archaeoglobus*, *Ferroglobus*	Atomi (2002) and Sato and Atomi (2010)
3-Hydroxypropionate/ 4-hydroxyburate cycle	**Green nonsulfur bacteria** *Chloroflexus* **Some sulfur-oxidizers** *Acidianus*, *Metallosphaera* **Others** *Archaeoglobus*, *Nitrosopumilus*	Atomi (2002), Hügler et al. (2003) and Sato and Atomi (2010)
Reductive tricarboxylic acid cycle	**Green sulfur bacteria** *Chlorobium*, *Chlorobaculum* **Some hydrogen-oxidizers** *Hydrogenobacter*, *Aquifex* **Some sulfate-reducers** *Desulfobacter* **Some sultirr-reducers** *Thermoproteus*	Atomi (2002), Tang and Blankenship (2010) and Agarwal et al. (2017)
Carboxylases	**Methanogenic archaea**	Thauer et al. (2008) and Agarwal et al. (2017)

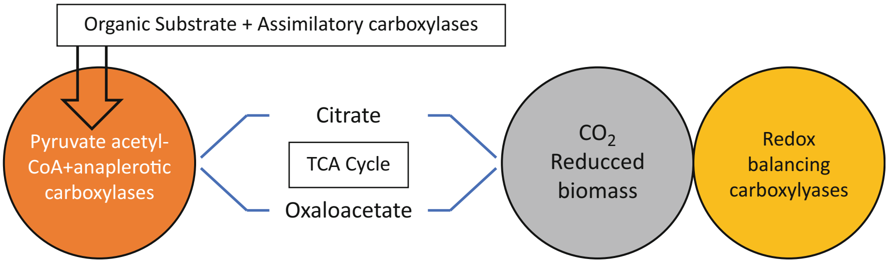


Fig. 4 Carboxylases cycle

In this pathway, carboxylating enzymes incorporate inorganic C into pyruvate, acetyl-coenzyme A (acetyl-CoA), or citric acid cycle (tricarboxylic acid [TCA] cycle) intermediates (Erb 2011). However, in heterotrophy, the organism utilizes organic source of C rather than fixation of inorganic C. However, for some substrates, carboxylation is a necessity for making organic C available after degradation and transformation of biomass for utilization. Accordingly, carboxylases which are involved in heterotrophic pathways, permitting transformation of organic substrate into TCA cycle intermediates, are referred as assimilatory carboxylases (Fig. 4). Once the metabolites are formed, they are taken for biosynthesis which results in the reduction of TCA intermediates. They are produced via TCA cycle to overcome the deficiency of these intermediates. A large number of organisms including those that do not rely on the action of autotrophic or assimilatory carboxylases adopt the anaplerotic reactions that mostly utilize carboxylation reaction (Kornberg and Krebs 1957; Kornberg 1965). Prime carboxylation examples are the synthesis of polypeptide and fatty acids as secondary metabolites which require crucial carboxylation reactions. In both the pathways, α-carboxylations are required for activated acyl-CoA ester building blocks for C-C bond-formation reaction. In eukaryotes and bacteria biosynthesis, malonyl-CoA extender units for manufacturing of fatty acid chains are produced by carboxylation of acetyl-CoA through biotin-dependent acetyl-CoA carboxylase. Addition of CO_2 is utilized to stimulate the acetyl-CoA molecule for elongation reaction: irreversible exclusion of CO_2 by decarboxylation which yields a reactive enolate anion. It serves as a nucleophile to spread the growing C chain in a Claisen condensation-like manner (Tong 2005).

5 Major Enzymes Involved in Carbon Dioxide Fixation

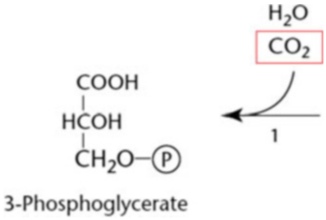
Enzymes involved in Calvin-Benson-Bassham cycle Rubisco, the key enzyme of the CBB cycle, have been examined in a wide variety of organisms. Based on primary structure, Rubisco proteins can be structurally divided into four types (Types I–IV), but those contributing to the CBB cycle are Type I or Type II enzymes.

5.1 Enzymes Involved in Calvin-Benson-Bassham Cycle

In all the plants, cyanobacteria, algae, and chemoautotrophs, dominant enzyme is Type I Rubisco. It has 2 subunits, i.e., large that has 50–55 kDa subunits and small having 12–18 kDa subunits. As compared to Type I, Rubisco Type II are present in bacteria. This enzyme is composed of large subunits (Hartman et al. 1984). *Thiobacillus*, *Rhodobacter*, and *Hydrogenovibrio* contain both Type I and Type II enzymes (Paoli et al. 1995).

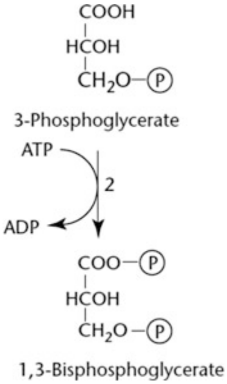
Ribulose-1,5-bisphosphate carboxylase/oxygenase

This enzyme is involved in the fixation of CO_2 and H_2O molecule in 3-phosphoglycerate.



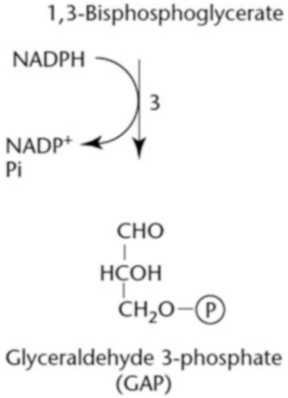
Phosphoglycerate kinase

It converts 3-phosphoglycerate into 1,3-bisphosphoglycerate by consuming ATP.

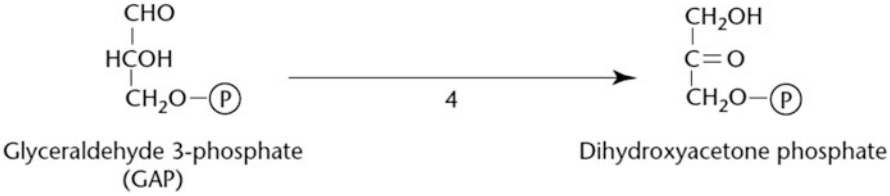


Glyceraldehyde-3-phosphate dehydrogenase

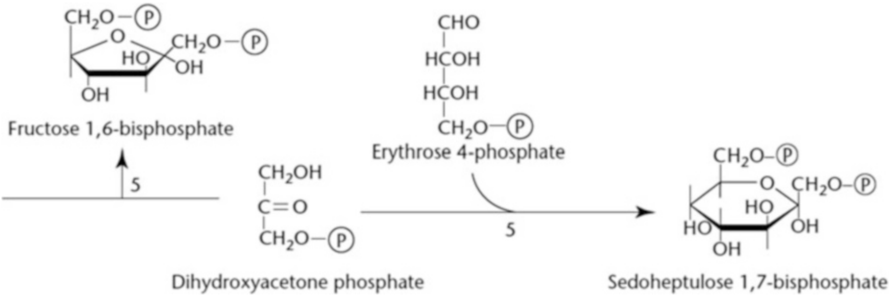
1,3-Bisphosphoglycerate is catalyzed by glyceraldehyde-3-phosphate dehydrogenase into glyceraldehyde 3-phosphate by using NADPH.



Triose phosphate isomerase
Involved in conversion of glyceraldehyde 3-phosphate into dihydroxyacetone phosphate.

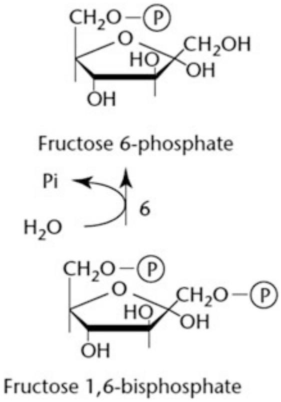


Fructose-bisphosphate aldolase
Dihydroxyacetone phosphate is either converted into fructose 1,6-bisphosphate or sedoheptulose 1,7-bisphosphate (addition of erythrose 4-phosphate).



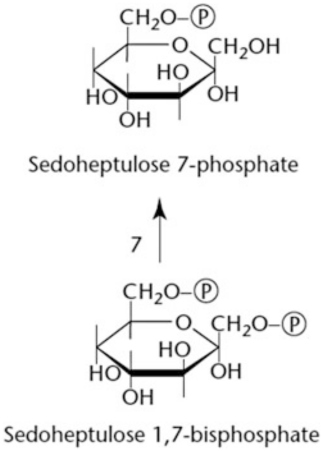
Fructose-1,6-bisphosphatase

This enzyme catalyzed fructose 1,6-bisphosphate into fructose 6-phosphate.



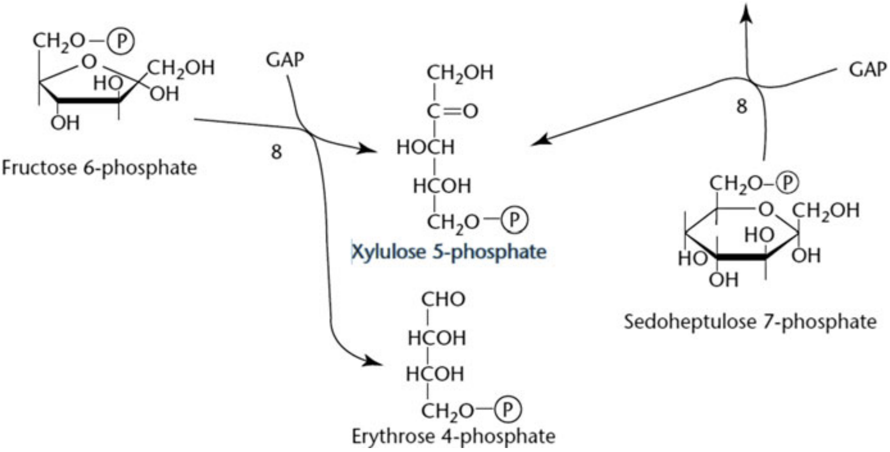
Sedoheptulose bisphosphatase

Involved in conversion of sedoheptulose 1,7-bisphosphate into sedoheptulose 7-phosphate.



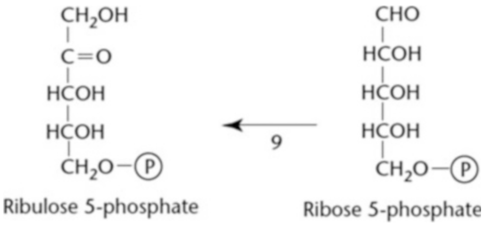
Transketolase

Fructose 6-phosphate and sedoheptulose 7-phosphate are catalyzed and changed into erythrose 4-phosphate and xylulose 5-phosphate, respectively.



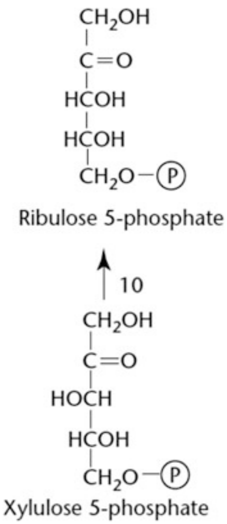
Ribose-5-phosphate isomerase

This enzyme is involved in conversion of ribose 5-phosphate into ribulose 5-phosphate.



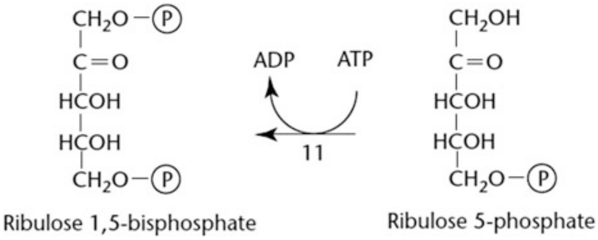
Ribulose-5-phosphate 3-epimerase

This enzyme change xylulose 5-phosphate into ribulose 5-phosphate.



Phosphoribulokinase

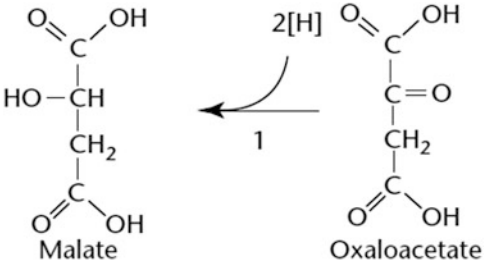
Phosphoribulokinase catalyzed ribulose 5-phosphate into ribulose 1,5-bisphosphate to start Calvin-Benson-Bassham cycle again (Sato and Atomi 2010).



5.2 Enzymes Involved in Reductive Tricarboxylic Acid Cycle

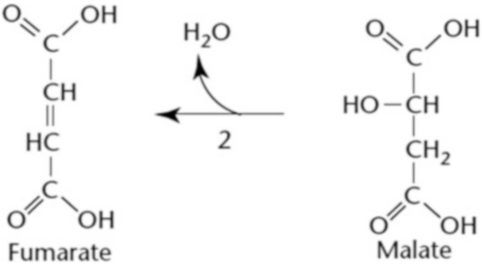
Malate dehydrogenase

This enzyme is involved in conversion of oxaloacetate into malate.



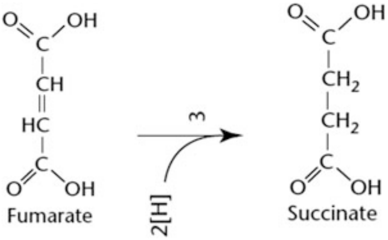
Fumarate hydratase

Malate is converted into fumarate by catalytic activity of fumarate hydratase.



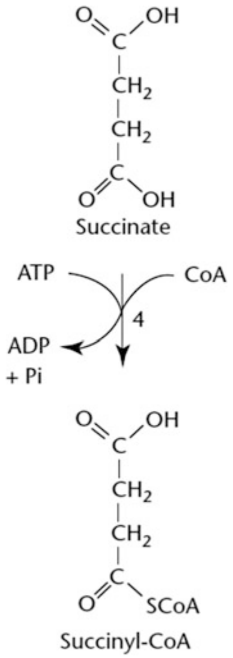
Fumarate reductase

Fumarate is changed into succinate via activity of fumarate reductase.



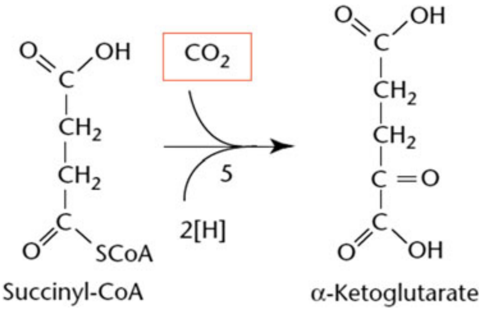
Succinyl-CoA synthetase

This enzyme catalyzed succinate into succinyl-CoA.



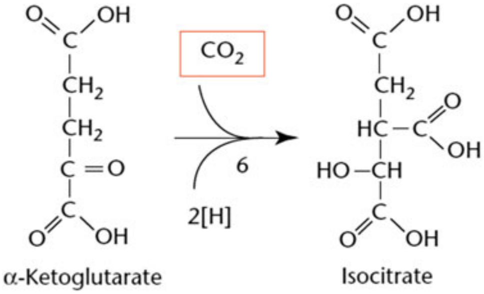
Oxoglutarate synthase

Succinyl-CoA is changed by addition of CO_2 into α-ketoglutarate under activity of this enzyme.



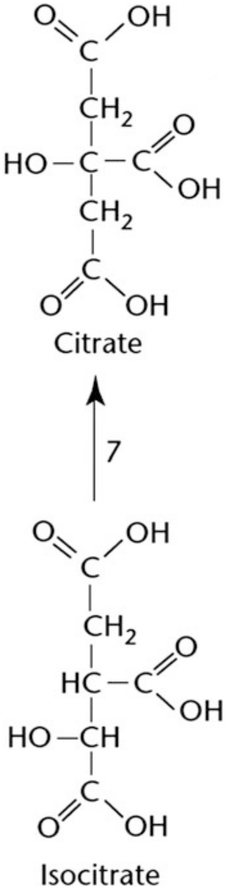
Isocitrate dehydrogenase

Addition of CO_2 into α-ketoglutarate changed it into isocitrate, and reaction is catalyzed by isocitrate dehydrogenase.

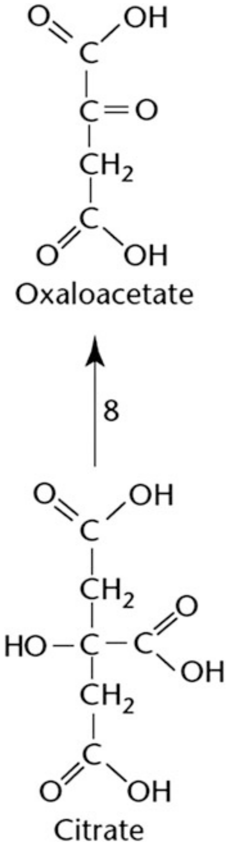


Aconitate hydratase

Aconitate hydratase catalyzed isocitrate into citrate.



ATP-citrate lyase
ATP-citrate lyase changed the citrate into oxaloacetate to start the cycle again (Sato and Atomi 2010).

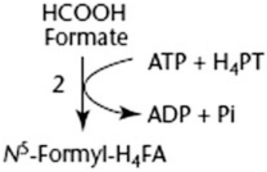


5.3 Enzymes Involved in Reductive Acetyl-CoA Pathway

Formate dehydrogenase
It is involved in addition of CO_2 to make formate by acetogen.

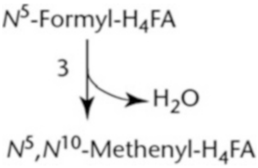
Formyl-h4fa-synthase

This enzyme catalyzed the conversion of formate into N5-formyl-H4FA.



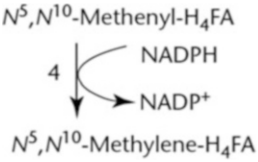
Methenyl-h4fa-cyclohydrolase

N5-Formyl-H4FA is changed into N5, N10-methenyl-H4FA by removal of a water molecule via activity of methenyl-h4fa-cyclohydrolase.



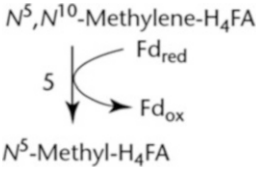
Methylene-h4fa-dehydrogenase

This enzyme changed N5, N10-methenyl-H4FA into N5, N10-methylene-H4FA.



Methylene-h4fa-reductase

N5, N10-Methylene-H4FA is converted into N5-methyl-H4FA under activity of methylene-h4fa-reductase.

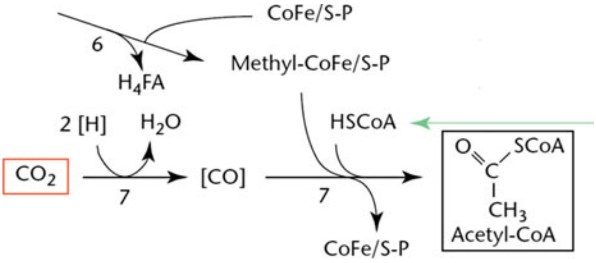


Methyltransferase

N5-Methyl-H4FA is catalyzed by methyltransferase into H4FA and methyl-CoFe/S-P.

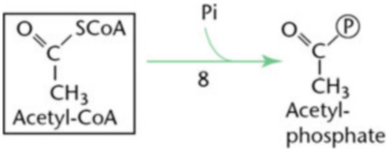
Carbon monoxide dehydrogenase/acetyl-CoA synthase

This enzyme is involved in addition of CO_2 to make acetyl-CoA.



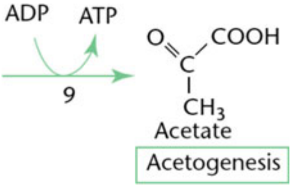
Phosphotransacetylase

Phosphotransacetylase catalyzed acetyl-CoA into acetyl-phosphate.



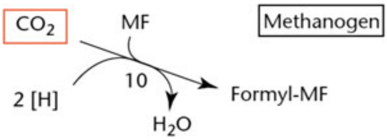
Acetate kinase

Acetyl-phosphate is catalyzed into acetate by acetogenesis.



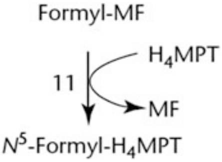
Formylmf dehydrogenase

Methanogen incorporate CO_2 to form formyl-MF by using formylmf dehydrogenase.



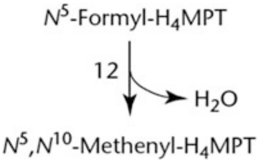
Formylmf:h4mpt formyltransferase

Formyl-MF is changed into N5-formyl-H4MPT by catalytic action of formylmf: h4mpt formyltransferase.



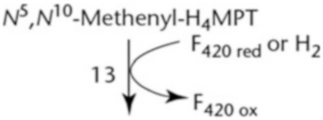
N5, n10-Methenyl-h4mpt cyclohydrolase

N5-Formyl-H4MPT after removal of water molecule under N5, n10-methenyl-h4mpt cyclohydrolase become converted into N5,N10-methenyl-H4MPT.



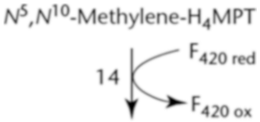
N5, n10-Methylene-h4mpt dehydrogenase

N5,N10-Methenyl-H4MPT is catalyzed by N5, n10-methylene-h4mpt dehydrogenase into N5,N10-Methylene-H4MPT.



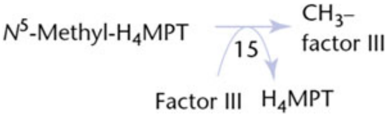
N5, n10-methylene-h4mpt reductase

This N5,N10-methylene-H4MPT is further catalyzed by N5, n10-methylene-h4mpt reductase and changed into N5-methyl-H4MPT.



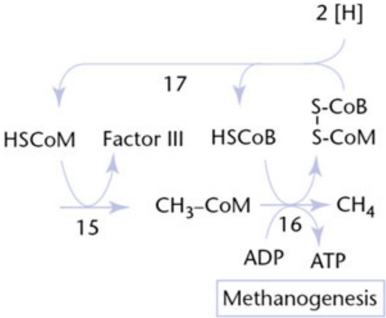
N5-Methyl-h4mpt:coenzyme m

N5-Methyl-H4MPT is converted into CH3- factor III and then CH3 − CoM by N5-methyl-h4mpt:coenzyme m.



Methyltransferase, methyl-coenzyme m reductase and heterodisulfide reductase

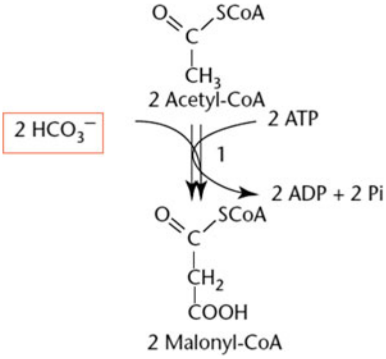
Methyltransferase, methyl-coenzyme m reductase and heterodisulfide reductase after a series of reaction finally complete the cycle. This final reducing reaction is catalyzed by CoB-SH-dependent methyl-S-CoM reductase that cause emission of methane.



5.4 Enzymes Involved in 3-Hydroxypropionate/4-Hydroxybutyrate Cycle

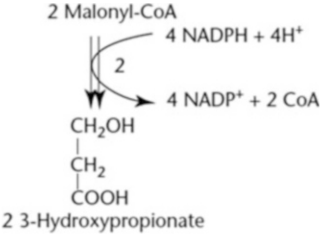
Acetyl-CoA carboxylase

This enzyme played an imperative role in conversion of acetyl-CoA into malonyl-CoA.



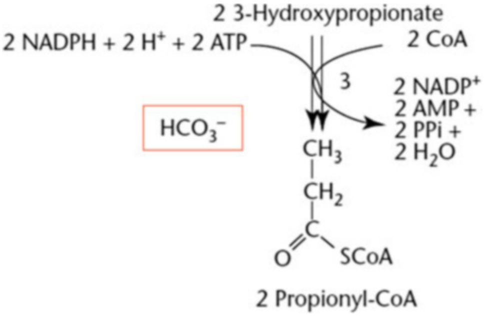
Malonyl-CoA reductase

This enzyme catalyzed malonyl-CoA into 2 3-hydroxypropionate.



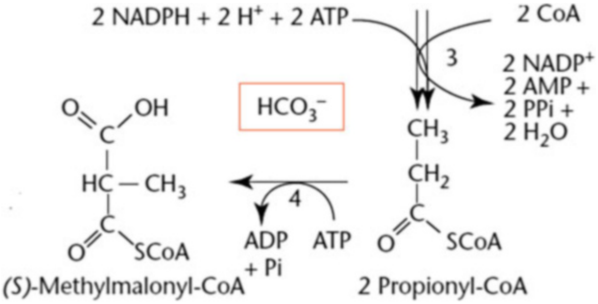
Propionyl-CoA synthase

2 3-Hydroxypropionate is converted into 2 propionyl-CoA under this enzyme.



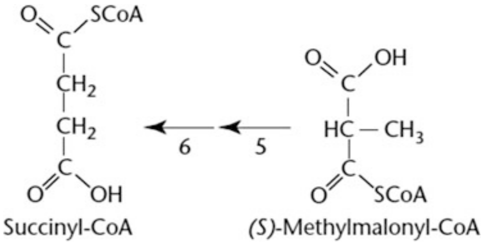
Propionyl-CoA carboxylase

2 Propionyl-CoA is catalyzed into (S)-methylmalonyl-CoA by propionyl-CoA carboxylase.



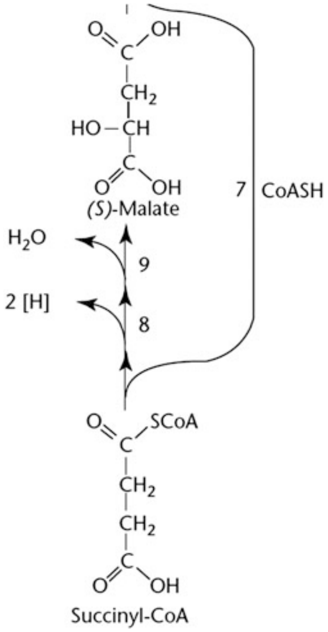
Methylmalonyl-CoA epimerase and methylmalonyl-CoA mutase

(S)-Methylmalonyl-CoA is converted into succinyl-CoA via activity of methylmalonyl-CoA epimerase and methylmalonyl-CoA mutase.



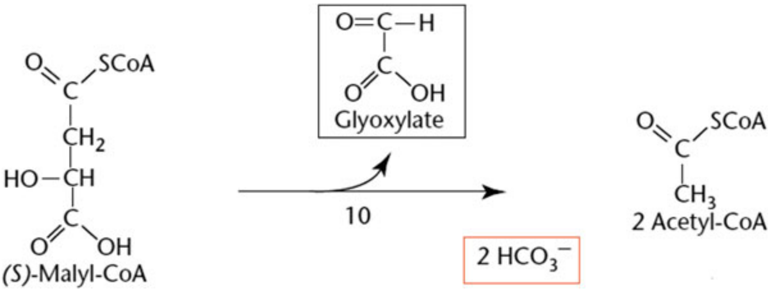
Succinyl-CoA:(S)-malate-CoA transferase, succinate dehydrogenase, and fumarate hydratase

Succinyl-CoA is changed into (S)-malate and (S)-malyl-CoA by catalytic activity of succinyl-CoA:(S)-malate-CoA transferase, succinate dehydrogenase, and fumarate hydratase.



(S)-Malyl-CoA

(S)-Malyl-CoA released a molecule of glyoxylate and finally changed into 2 acetyl-CoA by(S)-malyl-CoA.



6 Microbial Cell Components' Role in Carbon Stabilization

Glomalin

Glomalin is an insoluble, recalcitrant, and hydrophobic glycoprotein which is resistant against degradation (Wright and Upadhyaya 1996). It produces a "lattice-like waxy coating" that makes soil particles, sand, organic matter, clay, and silt sticky to start complex process aggregation in soil. It can accumulate more than 5% of soil C and nitrogen, thus saving the carbonaceous compounds against degradation and providing resistance against water and wind erosion (Emran et al. 2012; Meena et al. 2018). Thus, glomalin plays an efficacious role in maintaining soil C pool and formation of aggregate and increasing organic contents (Plaza et al. 2013). Soil aggregation and soil organic matter (SOM) further upholds nutrient storage capacity, microbial diversity, and water-holding capacity, ultimately determining the soil fertility and soil health (Wu et al. 2014; Gupta and Germida 2015). Glomalin production by arbuscular mycorrhiza fungi (AMF) largely depends on the plant productivity and photosynthate allocation (Fig. 5). The more dependent a plant is on mycorrhizal symbiosis for nutrient uptake, the more C is allotted to AMF by plant in the form of photosynthate making plants a major factor governing glomalin production (Treseder and Allen 2000). Increase in plant growth rate and nutrient content has shown a positive effect on glomalin production (Violi et al. 2007).

Hydrophobin

Fungal hydrophobin is a family of low molecular weight proteins (100 amino acids) consisting of four disulfide bridges and an extraordinary hydrophobic patch (Wösten

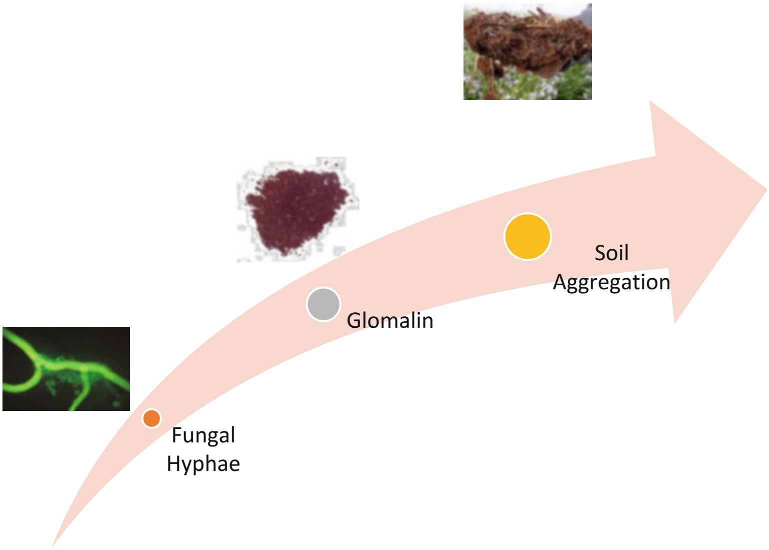


Fig. 5 Soil aggregation by lattice-like waxy coating produced by glomalin

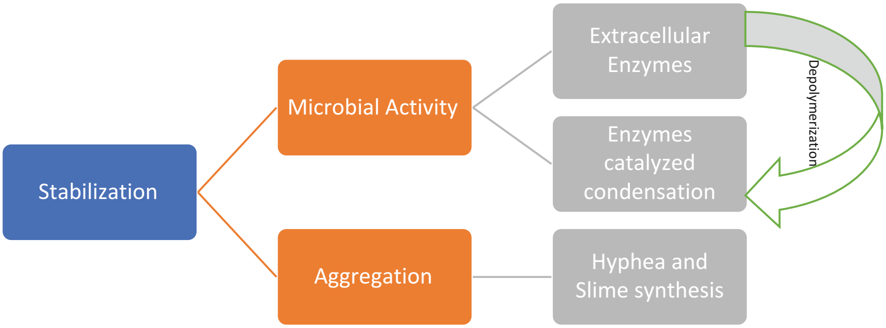


Fig. 6 Microbial cell components in carbonstabilization

2001). They were first discovered and separated in *Schizophyllum commune* in 1991 (Khalesi et al. 2015; Sunil et al. 2018). Hydrophobin are not alike, yet have eight conserved cysteine residues. The hydrophobic patch of hydrophobins and the molecules of gaseous CO_2 may interact together and form the stable CO_2-nanobubbles covered by an elastic membrane (Fig. 6).

Chaplins

These are produced exclusively by gram positive bacterial domain streptomycetes (phylum *Actinobacteria*), conferring hydrophobic properties to surfaces. The chaplins share a hydrophobic domain of ~40 residues (chaplin domain), and all have a secretion signal. Mass spectrometry of cell wall extracts confirmed that the short chaplins localized to the cell surface (Sunil et al. 2018). All chaplins are as precursors with an N-terminal signal sequence and a short hydrophobic domain (chaplin domain) of about 40 residues. Chaplins D to H are small polypeptides, whereas chaplins A to C are larger and carry a C-terminal sorting signal (LAXTG motif). Deletion of six chaplin genes (chpA to -H) hindered the formation of aerial hyphae, and the defect could be rectified by the addition of purified chaplin proteins (Claessen et al. 2003).

7 Conclusion

CO_2 fixation is the most important and effective reaction on the planet. We are not fully aware of the current status and extent of chemolithoautotrophy on the earth surface. Ecosystems of groundwater, especially with organic pollution, exhibit CO_2 fixation. They are contributing a lot toward global C economy. Autotrophs construct their cell mass merely from inorganic form of C. That is why, autotrophs are taken as pivotal part of the planet C cycle. The organic C is used by heterotrophs. They oxidize the C and send it back to the atmosphere. So the cycle completes accordingly. Balanced levels of CO_2 and oxygen are due to the balance between autotrophy and heterotrophy. This is how redox equilibrium on the planet is maintained.

CO_2-fixing microorganisms are basically connected in forming complexes of inorganic CO_2 with caceous organic entities. A wide range of bacteria and archaea have been found to be fixing C dioxide. They adopt six pathways. These CO_2-fixing microorganisms are specific in nature and are inhabitants of a variety of aerobic and anaerobic environments. Autotrophic microbes, though not fully explored, possess a great deal of capability to fix CO_2 into organic substances using energy from sunlight and/or inorganic chemical entities with electron donating attributes. Certain biochemicals and fuels are synthesized resultantly. Productivity of these biochemical and fuels have been enhanced through modifications in synthesis pathways and engineering at genetic level. Interestingly, techniques of altered pathways of synthesis of biofuels and energy harnessing systems are being transplanted in heterotrophs. Attention is being paid currently on electro-catalysts and light capturing semiconductors to be used in these modifications. It would lead to a highway to the increased microbial potential of CO_2 fixation. As far as CO_2 fixation by the bacteria affected by field crops is concerned, long-term cropping systems have been found better to increase CO_2 fixation as compared to rotations. Rice-rice cropping system is better than rice-rapeseed and rapeseed-maize crop rotation. In these cropping systems, certain bacterial species were found to be abundant to be contributing in CO_2 fixation. Some of the non-photosynthetic bacteria have potential to fix CO_2. The species of bacteria vary with change in electron donor; certain acetogenic bacteria are basically obligate anaerobes that have potential to use CO_2. This CO_2 is available in anaerobic environments. The acetogenic bacteria use CO_2 as terminal electron acceptor and resultantly synthesize acetate and other fatty acids. There are two groups of acetogenic bacteria that have been observed. The first group reducing equivalents for reduction are synthesized by oxidizing H_2, CO, formate or other one-carbon compounds, carbohydrates, alcohols, organic acids, amino acids, and purines. They have a great variety in metabolism, so they can use a variety of reduced substances. They are abundant in all of the non-marine environments which are anoxic. Their isolation techniques have been devised too. The second group of these acetogenic bacteria is with specific metabolism, which involves fermentation of purines and some of the other bio-entities, especially amino acids. This group transfers very small number of reducing equivalents to CO_2. Scientists intrigued by cyanobacteria for multiple reasons. Cyanobacteria have developed mechanism to survive and flourish in a variety of environmental conditions. They can live anywhere. They carry out photosynthesis using light, H_2O, and CO_2 with the release of oxygen. Oxygenic process of photosynthesis through cyanobacteria has been exerting a great effect on atmosphere and natural cycles of C for billions of years.

8 Future Prospective

In view of above conclusion, research and development endeavors are to be continued to look for new C fixation bacterial species that would be more efficacious and resilient under changing climate change. In the foreseeable future, work on discovery of new pathway would be a demand of time to understand the microbial C fixation in depth and increase their efficacy in this regard. There is an urgency that research and development are to be boosted up to assimilate the increasing level of CO_2 and its fixation for sustainable management of climatic conditions. Region-wise strategies should be developed and implemented. Simulation models would be useful in determining the influence of microbes and C fixation for future climate change.

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Adsorption: An Important Phenomenon in Controlling Soil Properties and Carbon Stabilization

Omari Sufian

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Abstract

The global greenhouse gas emission rapidly rises every year, and its impact on climate change is evident with no doubt. Soil being a major sink of atmospheric carbon dioxide (CO_2) has attracted much attention to researchers studying ways it can be well managed to mitigate the issue of climate change. Several studies are undertaken with the aim to reveal the mechanisms through which soil minerals interact and hence adsorb organic carbon (OC). As a result, it is well established that soil plays a significant role in the control of the global carbon cycle through sorption of OC and stabilizing it. However, when soil is not well-managed, mineralization causes the release of OC, resulting in an increase of the CO_2 to the atmosphere. This calls for the need to understand the mechanisms through which OC-soil mineral associations can be maintained.

Keywords

Carbon stabilization · Soil clay minerals · Climate change · Global warming · Organic carbon

Abbreviations

CO_2	Carbon dioxide
CMI	Carbon management index
C	Carbon
CEC	Cation exchange capacity
CP/MAS^{13}C-NMR	Cross polarization-magic angle spinning carbon-13 nuclear magnetic resonance
DOC	Dissolved organic carbon
EDTA	Ethylenediaminetetraacetic acid
GDS	Great Dismal Swamp
HSI	Hue-saturation-intensity
MOA	Metal Organic Acid Association
NanoSIMS	Nanoscale secondary ion mass spectrometry
NOM	Natural organic matter
N	Nitrogen
OC	Organic carbon
OM	Organic matter
PHA	Peat humic acid
PES	Polymeric extracellular substances
PZC	Potential at zero charge
SSDOC	Sewage sludge dissolved organic carbon
SOC	Soil organic carbon
SSA	Specific surface area
SR	Suwannee River
WEOC	Water-extractable organic carbon

1 Introduction

Although there are a considerable slowdown on the annual rates of global carbon dioxide (CO_2) emissions since 2012, still 2015 was the hottest year over the history since 1880 when the global temperature records began (Olivier et al. 2016). Moreover, globally in 2016, the total emission of CO_2 a greenhouse gas continued to increase at the rate of 0.5–1% (Meena et al. 2018a, b; Olivier et al. 2017). Though efforts taken to mitigate global CO_2 emissions are highly encouraging, still the consequences of the emissions are extremely evident currently, and it seems the situation will not revert in the near future even if the top emitters fulfill their obligations on climate-related actions of 2020 within the context of the Paris Agreement. Soil can be a major source or sink of the atmospheric CO_2. Soil becomes a sink through the interaction of soil minerals with organic matter (OM) where bonds are formed and lock up organic carbon (OC). In a meanwhile, soil can act as a source of CO_2 through mineralization of OC locked up in the soil clay minerals. The respiration process of soil microbes affects soil carbon dynamics by releasing OC to the atmosphere in the form of CO_2. Soil microorganisms have an important role in soil respiration as about 80–95% of the mineralization of carbon (C) is due to their microbial activities (Hassink 1994). Indeed, soils hold approximately three times OC than the atmosphere or terrestrial vegetation, and it is clearly understood that small fluctuations in C protected in the soil is likely to impose substantial variation to the concentration of CO_2 in the atmosphere (Eglin et al. 2010; Schmidt et al. 2011; Smith et al. 2008). Therefore, it becomes of significant importance to clearly understand the mechanisms through which soil minerals adsorb and stabilize SOM so as to keep pace with practices which promise to improve soil carbon stabilization and alleviate emissions of CO_2. Three mechanisms are available to stabilize OM in soils: (1) intrinsic chemical recalcitrance, (2) organo-mineral complex formation by the interaction of OM with metal and minerals ions, and (3) physical protection due to occlusion of OM in soil aggregates (Barré et al. 2014; Datta et al. 2017).

Several studies reveal chemical interaction (stabilization mechanism 2) to have a special role in soil organic carbon (SOC) stabilization (Mikutta et al. 2007; Schneider et al. 2010; Wagai and Mayer 2007) and protect it from biodegradation. For instance, Kalbitz et al. (2005) reported about 30% decrease in mineralization when DOC adsorbed by the B horizon subsoil compared to mineralization occurring in the soil solution. Oxides and clay minerals available in soils are of great importance for adsorption and retain OM. Soil OM is effectively adsorbed and protected by iron oxides besides other clay minerals (Kaiser and Zech 2000a; Kaiser et al. 2007). Phyllosilicates a clay mineral are also reported to have a significant role in the stabilization of SOM (Balcke et al. 2002; Meena et al. 2020b; Kahle et al. 2004). Nevertheless, literature indicates that phyllosilicates adsorb much lower amount of OM compared to oxides (Chorover and Amistadi 2001; Kaiser and Guggenberger 2003). Fe/Al oxides in most acidic soils are reported to adsorb and consequently preserve larger amount of SOC than layer silicates, i.e., kaolinites and smectites (Chorover and Amistadi 2001; Kaiser and Guggenberger 2003). It is well-known that the amount of OC adsorbed by clay fractions is reduced when acidic soils have no Al/Fe oxides (e.g., Kaiser and Guggenberger 2000; Kaiser and Zech 2000b). Thus, Fe and Al oxide content determines the extent to which acidic soils protect SOC mineralization. For instance, more OC is adsorbed by $Al(OH)_3$ and goethite compared to kaolinite and illite (Kaiser and Zech 1999).

The main concern of this chapter is to understand the extent characteristic adsorption of soil minerals stabilizes SOM. The review starts by briefly discussing minerals available in soils and properties that enhance the adsorption of SOC. Then factors controlling adsorption of OC on mineral surfaces are presented followed by mechanisms involved to stabilize SOC. The studies analyzing the impact of soil mineralogy on the SOC stabilization are thereafter reviewed and finalize with the discussion on the extent warming climate may affect SOC stabilization.

2 Soil Clay Mineral Properties That Enhance Adsorption of Soil Organic Carbon

Intensive studies of soil phyllosilicates are available as in Refs. (Barré et al. 2014; Jackson 1964; Singh et al. 2018; Velde 1995; Wilson 1999) leading to many case studies, books, and reviews been documented. Therefore, present study does not focus to describe soil phyllosilicates per se but to provide some hints for the importance to consider soil phyllosilicate mineralogy to understand soil C dynamics. Variety of textbooks dedicated to extensively describe soil phyllosilicates can be referred as presented in Moore and Reynolds (1989) and Velde (1992). The phyllosilicates are small-sized (<5μm) crystal structures that significantly govern the properties of soil, and they are extremely diverse. Due to this fact, it is therefore necessary to understand their structure which eventually influences their properties for SOC retention. Soil phyllosilicates originate from transformation of minerals in water-rock interaction and neosynthesis and from parental materials. The important common phyllosilicates can be categorized into two main groups which are 1:1 kaolinitic and 2:1 vermiculitic and smectitic soil layers (Fig. 1a, b). The structure of 1:1 kaolinite layer consists of the apical oxide ions on the tetrahedral shared with octahedral sheet. The 2:1 layer types consist of an octahedral sheet covalently linked to cations in between two tetrahedral sheets. Lower charged cation substitutes a structural metal in a crystal lattice that results in the formation of a net permanently negative charge which is pH-independent on the siloxane surfaces. For instance, Al^{3+}or Fe^{3+}can substitute Si^{4+}in the tetrahedral sheets, while Mg^{2+}can substitute Al^{3+}. In tetrahedral sites, the substitution of $Si^{4+}$by Al^{3+} having a lower charge or in octahedral sites ($Al^{3+}$by Mg^{2+}) results in a layer silicate to acquire a net "permanent" negative charge (Fig. 1c, d). Then the charge in the layer silicate is counterbalanced by adsorption of cations from the solution to maintain electroneutrality (Alekseeva 2011; Bolan et al. 1999; Churchman and Lowe 2012). Isomorphic substitution is common in 2:1 clay layers and renders a negative charge which is permanent on their surface, whereas they are less common in 1:1 clay layer. This results in 1:1 clay layers being not always permanently charged. Depending on the soil pH hydroxyls on the broken edges are ionizable causing 2:1 and 1:1 clay minerals to have variable

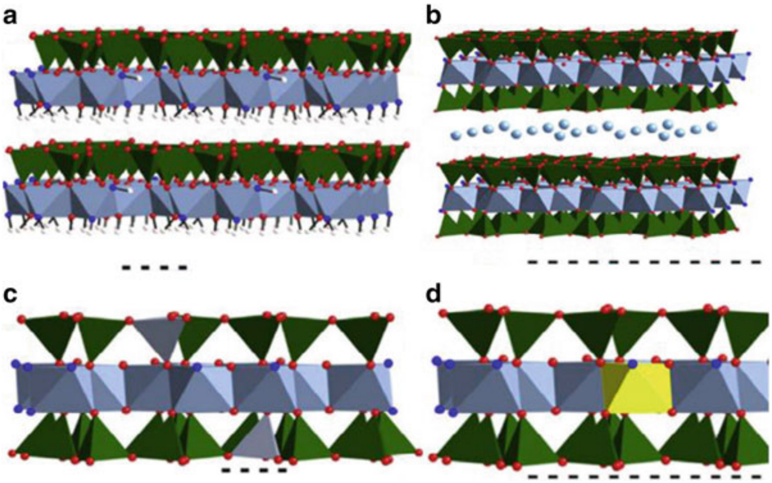

Fig. 1 (**a**) Structure of kaolinite indicating octahedral (blue-gray) and tetrahedral layers (green), (**b**) structure of montmorillonite with Ca^{2+} ions in the interlayer, (**c**) the tetrahedral layers with a lower charged Al^{3+} substitutingSi^{4+}, (**d**) the octahedral layer of a negatively charged siloxane surfaces resulting due to Mg^{2+} substituting Al^{3+}. (Adopted from Kleber et al. 2015)

Table 1 Soil clay mineral properties

Group name	Type	Name	Surface area (m^2 g^{-1})	Cation exchange capacity (c mol g^{-1})	Distinctive physical properties	Stability
Kaolin	1:1	Kaolinite	6–40	0–8	Platy	Quite high
Mica	2:1	Illite	55–195	10–40	Platy	Moderate
Smectite	2:1	Montmorillonite	650–800	80–120	Swell	Low
Vermiculite	2:1	Vermiculite	600–800	120–150	Swell	Low
Al–Si	2:1	Allophane	700–1500	pH variable	Amorphous	Low to moderate

Adopted from Huang et al. (2011)

charges which are pH-dependent. These are the only characteristic charges for 1:1 clay layers. Table 1 summarizes the properties of some common phyllosilicate minerals.

Another type of soil mineral is metal (Fe/Al) oxides which have demonstrated to be effective in C adsorption and stabilization in the soil. These oxides are reactive sites characterized by a range of O and OH groups which particularly occur in many neutral and acidic soils. Fe oxides determine the soil color even when they exist in trace amount. Also, through concretion and cementation of other clay minerals, Fe oxides form stable aggregates. In Table 2 some of the common oxide and hydroxide minerals are shown with their characteristics. Goethite (α-FeOOH) is the most

Table 2 Some common oxides and hydroxide minerals showing their properties

Common soil minerals	Chemical formula	Specific surface area (m^2g^{-1})	Soil characteristics	Soils of common occurrence
Goethite	α-FeOOH	14–77	Yellow brown color	Iron oxide mostly widespread
Hematite	α-Fe_2O_3	35–45	Bright red color	Mostly soils in warmer places
Ferrihydride	$Fe_5OH_8.4H_2O$	200–500	Spherical particles, pinkish to yellowish-red color	Characteristics of soil where Fe(II) is rapidly oxidized
Magnetite	γ-Fe_2O_3	Not well-known, probably high	Ferrimagnetic	Tropical or subtropical soils, possibly from bacteria, fires

Adopted from Churchman and Lowe (2012)

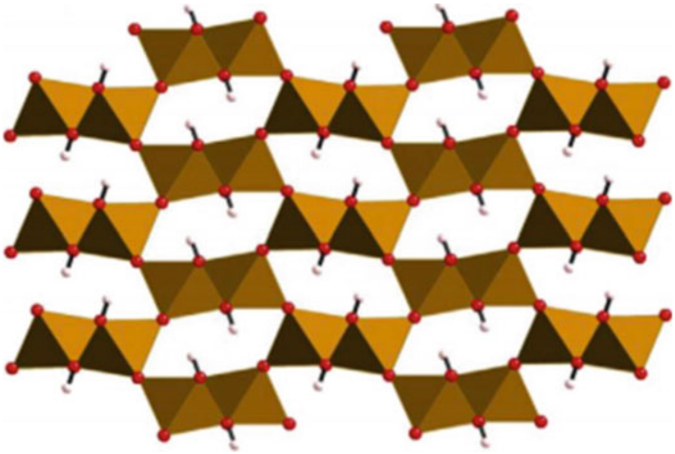

Fig. 2 Structure of goethite (α-FeOOH) with dioctahedral $Fe(OOH)_6$, oxygen are shown as red and hydrogen as white balls. (Adopted from Lehmann and Kleber 2015)

common Fe oxides in soils, and its presence makes soils appear dark reddish-brown in color (Fig. 2). Other common Fe oxides are magnetite (γ-Fe_2O_3), ferrihydrite ($Fe_5OH_8.4H_2O$), and hematite (α-Fe_2O_3) which gives soils a bright red to pink color. The average content of Fe oxide in soil ranges from 1 to 500 g kg^{-1}. As shown by their thermodynamic stabilities, hematite and goethite are usually in conditions where respiration occurs at limited supply of oxygen (Huang et al. 2011). The cation exchange capacity of all Fe oxides depends on soil pH. In soils there are several crystalline oxides, oxyhydroxides, and hydroxides of aluminum. The most common of these in soils is gibbsite, $Al(OH)_3$, which form a major constituent of minerals in Oxisols and Ultisols. The Al^{3+} ions are coordinated in octahedral and join together hydroxyl sheets which make the gibbsite layer. Of the possible unoccupied cathedral interstices, aluminum ions occupy two-thirds of them. The hydroxyl ions in adjacent layers are almost directly opposite to each other (Loveland 1983), and hydrogen bonds hold together layers in between opposite OH groups. Gibbsite among the oxides of Al, particularly, is important in the soil aggregate formation though the mechanisms are not well understood.

3 Control of Organic Carbon Adsorption on Mineral Surfaces

3.1 Soil Conditions

Soil conditions determine to what extent minerals stabilize OC, as, for example, soil pH is a determinant of the extent OC is stabilized in acidic soils (Mayer and Xing 2001). Shifting of soil pH and oxidation-reduction environment can be induced by change in the condition of the soils, which subsequently alter the soil reactive minerals, including iron (Fe) and aluminum (Al) oxides regulating both SOM stored and available (Berhe and Kleber 2013). The site density on the surface of the hydroxyl groups of minerals determines their pH-dependent charge status and the extent pedogenic oxides react. More negative charged surfaces are observed when the pH is increased beyond their point of zero charge (normally for most Fe and Al oxides between 7.5 and 9), while oxides are rendered more attractive toward negatively charged soil organic compounds when pH decreases due to protonation of their surface hydroxyls (Berhe and Kleber 2013). Furthermore, texture is among crucial soil condition for the adsorption of OC. The organic matter in coarse-textured soils decomposes relatively faster than available in fine-textured soils (Hassink 1992). This may be attributed by OC being physically protected against microbial attack by fine-textured soils (Hassink 1995). Almost in every land use, the texture of the soil is important in the preservation of organic matter (e.g., in cropland, forest land, shrub land) in the lower soil depths (Albaladejo et al. 2013; Fontaine et al. 2007). Microbes in clay-dominated soils do not easily access soils' organic C compared to sandy soil. This is probably due to physical occlusion within microaggregates and also surface of phyllosilicates minerals which adsorb organic matter chemically (Sissoko and Kpomblekou-A 2010). Soil organic carbon and soil structure are interrelated such that SOC form aggregates through holding minerals together in soils and in turn aggregates protect SOC against mineralization (Elliott 1986; Gupta and Germida 1988; Tisdall and Oades 1982). Soil aggregates with relatively low stabilities (e.g., cultivated soils/coarse-textured) have lower capacity to stabilize OC compared to aggregates from natural ecosystems like fine-textured soil or those from reduced tillage (Borchers and Perry 1992; Hassink 1992). The soil's ability to adsorb, protect, and retain OC is usually influenced by soil moisture (Lamparter et al. 2009; Meena et al. 2020). For the biogeochemical functioning, the importance of water can be inferred by making comparison of the extent moisture has been distributed over the global, soil pH, and net primary production. For plants to produce biomass through fixing carbon, its growth should be sustained by adequate supply of soil moisture. Organic acids released by microbial processes of

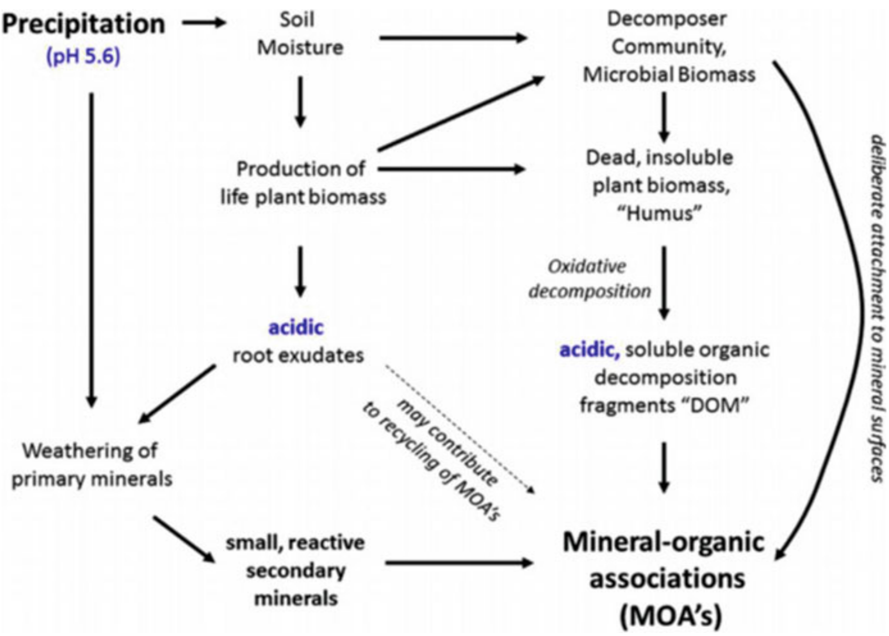

Fig. 3 The interdependence between moisture supply, mineral weathering, plant biomass production, and the formation of MOAs. (Adopted from Kleber et al. 2015)

oxidative decomposition and living roots lower soil pH and provide a media to mediate dissolution of minerals. This results in a strong causal relationship between soil moisture, soil pH, and biomass production as demonstrated in Fig. 3. According to this interrelation, Kleber et al. (2015) identified five factors facilitating the formation of mineral organic acid association (MOAs) in soil environments:

(i) Water is essential for life processes, providing the medium for transportation of dissolved or colloidal OM, microbes, and medium for reactions. The transport pathways and life process conditions widely differ between soils with ability to hold more organic carbon and saturated bulk soil and most preferred flow paths.

(ii) The plants through photosynthesis assimilate CO_2 and water to produce biomass; in turn when plant biomass dies, it provides substrate for microbial life. The host rock is physically disintegrated by roots and release polysaccharides, acids derived from organic matter, protons, plant amino acids, and other organic compounds, which through weathering contribute to soil formation and yield small organic matter and soluble molecules, which come to be part of the soil solution or exert directly a chemical reaction with mineral surfaces. Furthermore, exudates of plant root attract and support larger number of microbes in the region of the soil close to plant (rhizosphere).

(iii) The size of larger plant biopolymers is reduced by microbiota into smaller units, more soluble, oxidize and result to more functional groups attached to

OM. Oxidative depolymerization is the processes leading to depolimerization and functionalization which frequently occur together (Essington 2004). The organic acids, polymeric extracellular substances (PES), and chelators are secreted by microorganisms contributing to the pool of dissolved OM in soil or directly be deposited on surfaces of minerals.

(iv) Reactive mineral components derived from weathering products have high affinity to adsorption of OM due to large specific surface areas (SSAs). These include the nanometer-sized Fe oxides which are variably charged, short-range ordered Al-silicates (allophane and imogolite) and phyllosilicates a group of permanently charged ions.

(v) A soil media with low pH favors the formation of reactive minerals from weathering products and promotes strong inner sphere bonds formation (polar covalent bonds between structural surface atoms) between variable charge mineral surfaces (e.g., imogolite, Fe oxides, allophane, the edges of phyllosilicates) and OM. Probably in alkaline and neutral media, weaker outer sphere complexation (long-range Coulomb forces holding adsorbate electrostatically while at least one solvent molecule between itself and the surface retained) and hydrogen bonds dominate between OM and Fe oxides or phyllosilicates.

Contrarily, since in dry regions bonding strengths and abundances of MOAs are likely lower than of the soil in humid condition (more productive), it can be hypothesized that they are more prone to disturbance.

3.2 Management Practices

The management practices are important for soil health since it determines soil to function as either a sink or source of C. It is predicted about 40–80 Pg of C to be adsorbed in the soil over the next 50–100 years upon adopting management practices which are sustainable (Houghton 1996). The OC in the form of CO_2 is emitted into the atmosphere through mineralization due to poor optimum management practices causing deterioration of soil quality (Lal 2002). Controlled tillage operation and reducing cropping intensity can enhance adsorption of OC due to the decreased soil respiration rate (Paustian et al. 1992). When tillage is banned as a change from conventional management practices, the residence time of SOC in soil has been found to increase (Chivenge et al. 2007). Upon tillage the reasons causing the loss of protected SOC includes (a) leaching as dissolved C, (b) aggregates breaking causes mineralization of exposed C, and (c) water erosion or accelerated wind (Rhoton and Tyler 1990). More C is reported to be preserved and retained in soil by conventional tillage compared to other management practices since it forms stable aggregates (Devine et al. 2014; Follett 2001). Gains and losses of SOM are a function of several practices for management of soil including cropping system (Yadav et al. 2017) and cropping rate (Campbell et al. 1995; Engel et al. 2017; Novelli et al. 2017), application of fertilizer (Chaudhary et al. 2017; Gregorich et al. 1991; Purakayastha et al.

2008), reduced tillage (Devine et al. 2014; Lopez-Bellido et al. 2017; Reicosky et al. 1995), cultivation of grasses and perennial legumes (Campbell et al. 1991; Conant et al. 2017; Li et al. 2016), and also application of manure (Chaudhary et al. 2017; Cong et al. 2017; Sommerfeldt et al. 1988). Balanced fertilization, management practices, and proper cropping systems are mostly among the potential practices believed to increase SOC stock in agricultural soils (Lal 2002; Rudrappa et al. 2006; Shahid et al. 2017). The changes in agricultural management practices can influence the soil OC dynamics (Chivenge et al. 2007; Meena and Lal 2018; Purakayastha et al. 2008). Several practices causes the loss of SOC, including agricultural activities such as (a) excessive tillage, (b) deforestation, (c) fallowing, (d) drainage of wetlands, and (e) crop residues burning or removal (Lal 2002). Management practices which are friendly for OC adsorption includes conservation tillage, the application of integrated nutrient management, planting crops on slopes and contours, the use of farm wastes, precision farming, and crop rotation (Chaudhary et al. 2017; Collier et al. 2017; Lal 2003). Also, SOC can be reduced by clearing natural ecosystems for agricultural purposes. Generally, soil capacity to protect OC is impacted by management through two ways: (a) higher rates of loss and reduction of SOC due to cultivation and (b) decreased supply of inputs due to burning of crop residues and the C export during harvesting of plants (Engel et al. 2017; Koga et al. 2016; Novelli et al. 2017; Skjemstad et al. 2004; Sun et al. 2016). Ability of various strategies of soil management to adsorb and preserve the SOC is evaluated through carbon management index (CMI). The rate of change in the C dynamics of the soil system is compared to a reference soil which is more stable to enhance the determination of CMI (Brar et al. 2013). Carbon management index is a sensitive tool to monitor C dynamics variation between treatments with time on long-term basis. When a system is being rehabilitated, the greater CMI value is observed indicating improvement compared to system with lower CMI, depicting a decline.

4 The Mechanism of Soil Organic Carbon Stabilization by the Soil Minerals

Soil organic carbon stabilization is widely studied, and three mechanisms are proposed which are (i) physical, (ii) chemical, and (iii) biochemical/biological stabilization (please refer to Fig. 4 for details). Physical protection mechanism involves formation of aggregates which protect physically SOC by forming a layer which separates SOC and microbial enzymes, controlling food web interactions and subsequently the rate of microbial turnover (Edwards and Bremner 1967; Elliott 1986; Elliott and Coleman 1988; Jastrow 1996; Six et al. 2000; Tisdall and Oades 1982). Chemically SOC stabilization is achieved through physicochemical or chemical bonding of soil minerals with OC. As a result, this process leads to the organo-mineral complexes formation which is central to the protection of SOC against microbial attack. SOC stabilized by biochemical processes is realized through the formation of complexes which involves, for example, condensation reactions and recalcitrant resulting from compounds' own chemical composition (e.g.,

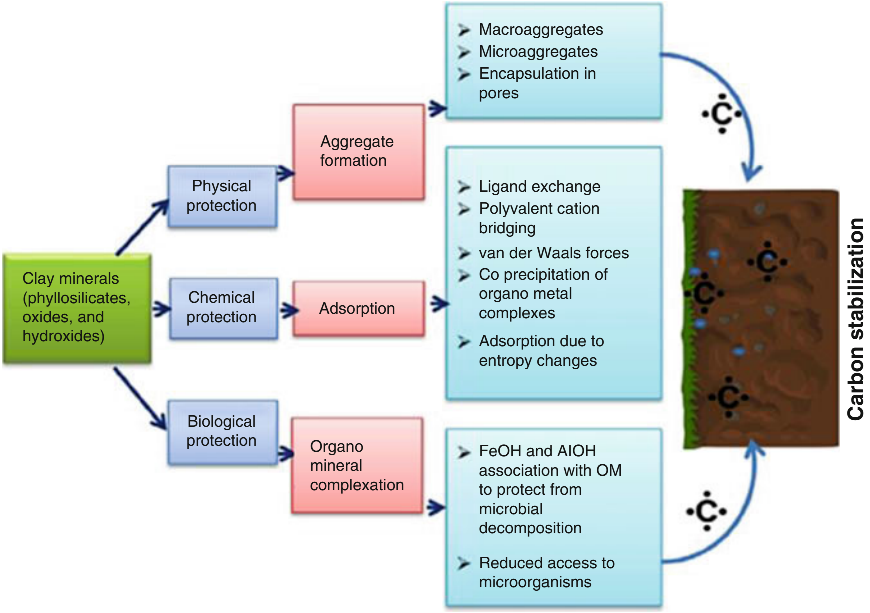

Fig. 4 Soil C stabilization mechanisms by clay minerals. (Adopted from Singh et al. 2018)

polyphenols and lignin). These mechanisms for SOC stabilization are further discussed in details in the next section.

4.1 Chemical Protection of Soil Organic Carbon

The SOM stabilization by clay minerals is well understood and reported in Feller and Beare (1997), Hassink (1997), and Sørensen (1972). For instance, Kalbitz et al. (2005) reported about 30% decrease in mineralization when DOC adsorbed by the B horizon subsoil compared to mineralization occurring in the soil solution. Several mineral phases such as amorphous and poorly crystalline with highly exposed functionalities such as hydroxyl groups greatly influences the stabilization of SOC through covalently bonding with OM and form mineral OM complexes (Lutzow et al. 2006). High chemical capacity of Fe and Al due to having hydroxyl functional groups exerts organo-mineral associations between hydroxyl groups and hydrophobic groups of OM.

Clay minerals, iron and aluminum oxides, hydroxides, and oxyhydroxides are of significant importance in sorption of DOC (Bolan et al. 2011; Singh et al. 2016). These oxides of Fe and Al, i.e., FeOx and AlOx, impacts SOM stabilization as evidenced by (a) their high sorption capacity (Tipping 1981), (b) a positive correlations between the concentrations of the total SOC and metal ions (Adams and Kassim 1984; Evans and Wilson 1985; Hughes 1982; Johnson and Todd 1983;

Kaiser and Guggenberger 2000; Kaiser et al. 1997; Skjemstad et al. 1990; Tiessen et al. 1984), (c) high ability to delay enzymatic/microbial mineralization of OM (Boudot et al. 1989; Jones and Edwards 1998), and (d) inverse correlations between their concentrations and SOC turnover rates (Masiello et al. 2004; Torn et al. 1997; Veldkamp 1994). In particular, Fe oxides hold special importance in the stabilization and sorption of SOC. Clay minerals, i.e., phyllosilicates, are also considered important in protecting DOC (Feng et al. 2005). Tombacz et al. (2004) reported that DO adsorption capacity of Fe (hematite and magnetite) is much higher compared to that of phyllosilicate under similar conditions. Also, Meier et al. (1999) found that at pH of 4.0 goethite adsorbed 0.25–0.3 mgC m^{-2} of DOC, while kaolinite adsorbed 0.08 mgC m^{-2}. Increasing pH causes to decrease the capacity of hydrous oxides to adsorb DOC (Gu et al. 1994). Low pH environments especially favor Fe oxides to protonate its functional groups and enhance binding of SOM by providing reactive surfaces. This is of great importance to enhance adsorption of DOC in strongly acidic forest soils.

Several studies are undertaken to investigate the SOM-Fe associations in the topsoil (Mueller et al. 2012, 2013; Remusat et al. 2012). The common practice has been use of nanoscale secondary ion mass spectrometry (NanoSIMS) offering high lateral resolution of around 100 nm to determine the microscale spatial relationships between SOM and Fe oxides. These studies successfully offered deep information at the submicron scale level compared to information typically analyzed using bulk soil samples. Nevertheless, in most studies only estimations were done to determine the duration which was required for the respective organo-minerals association formation. Recently, Dorau et al. (2019) conducted in situ analysis and provide evidence that Fe oxides are able to associate with soil organic matter in redox-variable condition within relatively short period of time (30 days). In the experiment, the redox bar was exposed to the soil solution only for the period in which the bars are installed (e.g., in this study 30 days) and thereafter record the conditions in the field environment. As a result though the redox bars were exposed in the field for rather short period of 30 days, on average SOM covered more than half of the Fe oxide surface, which highlight the important role of Fe oxide soil-dominated system to sequester SOM. Furthermore, increasing the amounts of dithionite-extractable Fe_d has been found to cause an increase in the amount of DOC adsorbed by the soil (Kaiser and Guggenberger 2000; Singh et al. 2016, 2017a, b). The quantity of OC adsorbed by clay minerals generally follows the order 1:1 clay minerals<2:1 clay minerals< oxides–hydroxides; probably CEC of the respective metals control the trend. Table 3 summarizes some selected studies on amount of OC adsorbed/desorbed by phyllosilicate minerals.

4.2 Biological Protection

Soil organic carbon protection by biological mechanism is related to the complex chemical molecular structure of the organic compounds due to their characteristics such as molecular conformation, elemental composition, and having some

Table 3 Summary of OC adsorption/desorption by various phyllosilicate minerals

Type of clay	Source C material is derived	Observations/inference	References
Illite, montmorillonite, polymeric Fe(OH), kaolinite	Two proteins, β-lactoglobulin (LG) and catalase (CA)	Though clay coated with polymeric oxyhydroxides of Fe has greater surface area, it has not in any way influenced significantly higher sorption of LG and CA than of the clean clays (homoioic to Ca^{2+})	Fusi et al. (1989)
Hematite and kaolinite	Humic/fulvic acids dissolved in groundwater	Humic acid was more firmly adsorbed on mineral surfaces than fulvic acid. Factors determining the content of humic acid adsorbed on mineral surfaces are content of hydroxyl groups on the minerals surfaces, humic acid properties, aromatic carbon content, and O/C ratio. Ligand exchange mechanisms explain humic acid adsorption mechanisms on two solid minerals since sorption increased with decrease in pH	Murphy et al. (1992)
Iron oxides	Fractionated NOM to hydrophobic (HbA), hydrophilic (HL), two sized fractions of <3 K and >3 K	At low pH media surface complexation-ligand exchange mechanism is involved in the preferential adsorption of NOM fractions rich in carboxyl/hydroxyl functional groups and aromatic C moieties by iron oxide surfaces. Specifically HbA fraction with large molecular weight was adsorbed in large quantity compared to small-sized HL fraction. Also fractions with >3 K were more adsorbed than those with <3 K	Gu et al. (1995)
Kaolinite and montmorillonite	Dissolved organic carbon extracted from sewage sludge (SSDOC)	Comparing mean Gibbs energy of adsorption (ΔGad) isotherms on a mass unit basis indicates that montmorillonite adsorbed much higher SSDOC than amount adsorbed by kaolinite	Baham and Sposito (1994)
Kaolinite and artificial Fe oxides,	DOC extracted from vinasse	DOC sorption decreases in the order kaolinite<	Benke et al. (1999)

(continued)

Table 3 (continued)

Type of clay	Source C material is derived	Observations/inference	References
i.e., hematite and goethite		hematite< goethite. The difference in sorption capacity of goethite and hematite may be due to their differences in geometries, while the low DOC adsorbed by kaolinite is due to its low PZC (pH) and SSA compared to hematite and goethite	
Goethite and kaolinite	Natural organic matter (NOM) from the Great Dismal Swamp (GDS) and Suwannee River (SR) water	The approximately maximum amount adsorbed was 0.30 mgC m^{-2} for SR goethite vs 0.mgC m^{-2} for SR kaolinite, GDS goethite, and GDS kaolinite	Meier et al. (1999)
Amorphous Al (OH)3, kaolinite, goethite, and illite	DOC from the forest floor	The DOC adsorbed by amorphous Al(OH)3 was 171 mmol kg,$^{-1}$ illite was 94 mmol kg^{-1}, goethite adsorbed 178 mmol kg^{-1}, and kaolinite adsorbed 102 mmol kg^{-1} When unit surface area analysis is considered, it is found that kaolinite adsorbed much higher DOC compared to illite which may be due to the greater contribution of octahedral sheet of the AlOH to the external surface areas	Kaiser and Zech (2000a)
Montmorillonite	Natural organic matter collected from Liberty Bay (Puget Sound, WA, USA) sediments and pore water natural organic matter	Increasing temperature results in the decrease in the sorption of NOM to the clay surfaces. Neither hydrophobic nor ion exchange mechanisms of OC adsorption were working in this system. The relative contributions for adsorption of natural organic matter in a $CaCl_2$ are approximately estimated to be 5% for cation bridging, 60% for van der Waals interactions, and 35% for ligand exchange	Arnarson and Keil (2000)
Fe and Al oxides, quartz kaolinite, illite, and montmorillonite	Humic acid	Reactive sites of smectitic and illitic clays has been blocked upon addition of goethite resulting in the	Zhuang and Yu (2002)

(continued)

Table 3 (continued)

Type of clay	Source C material is derived	Observations/inference	References
		decrease in their capacity to adsorb OC	
Amorphous Al (OH)3, ferrihydrite, gibbsite goethite, hematite, kaolinite, and illite	A field-fresh sample of OC extracted from the O horizon of a Haplic Podzol	The amount of OC adsorbed were 2.8 m^2 g^{-1}, 1.3 m^2 g^{-1} C, 17.2 m^2 g^{-1} C, 11.0 m^2 g^{-1} C, 4. m^2 g^{-1} C, 7.0 m^2 g^{-1} C, and 6.7 m^2 g^{-1} C for hematite, goethite, illite, gibbsite, kaolinite, amorphous Al(OH)3, and ferrihydrite, respectively	Kaiser and Guggenberger (2003)
Kaolinite, illite, and Ca-montmorillonite	DOC extracted from coniferous forest (pine) soil	In this study fractions of the soil clay adsorbed DOC between 9 and 44μg/m^2. Kaolinite strongly adsorbed large amount of DOC compared to illite, despite illite having a higher CEC and much larger SSA than kaolinite. Based on their SSAs, large amounts of DOC (44μg /m^2) were adsorbed by kaolinite while illite adsorbing a small amount, i.e., 9μg/m^2	Kahle et al. (2004)
Smectite, kaolinite system	Soil microbial exopolysaccharides represented by xanthan	Smectite exhibit as much as twice average sorption compared to kaolinite. A low charged smectite adsorbed large amount than kaolinite with a charged layer typically originating in the tetrahedral positions	Dontsova and Bigham (2005)
Montmorillonite (SAz-1) and kaolinite (KGa-1b) clay minerals	Peat humic acid (PHA) extracted from a Florida Peat sample	The rate of peat humic acid (PHA) adsorption increased with decrease in pH and as ionic strength increase. Based on surface area, the maximum adsorption of PHA was much higher on kaolinite (0.08–0.43 mgC/m^2) than on montmorillonite (0.006–0.06 mgC/m^2)	Feng et al. (2005)
Smectite, goethite, ferrihydrite, illite, and hematite and kaolinite	DOC extracted from truncatula, Medicago Praggio	Due to having higher CEC and SSA, smectite sorbed large amount of C compared to illite or kaolinite. The significance for differences in	Saidy et al. (2013)

(continued)

Table 3 (continued)

Type of clay	Source C material is derived	Observations/inference	References
		adsorption among all clays coated with goethite was observed only in kaolinite	
Illite a clay dominant in loamy sand mixed with kaolinite dominant in subsoil	Water-extractable organic carbon (WEOC)	Clays with low Fe/Al concentrations and higher TOC content exhibit lower sorption capacity. Also, SSA, CEC, and clay mineralogy had no impact on the adsorption of DOC	Nguyen and Marschner (2014)
Smectite a dominant clay mineral, with minor amounts of illite and kaolinite	Water-extractable organic C (WEOC) from mature wheat residue	At highest concentration of DOC added increasing rate of Ca^{2+} addition mainly increased adsorption of DOC. Also Ca^{2+} hold great role in binding organic matter to clay	Roychand and Marschner (2015)
Smectitic, allophanic, and kaolinitic-illitic	Water-extractable organic C (WEOC) from wheat straws	Soil isolated clay fractions were used to conduct experiments of DOC adsorption-desorption. DOC sorption decreased as kaolinite–illite < allophane < smectite. Adsorption of DOC increased as background electrolyte concentration increase. Also, possibly due to cationic bridging effect, the Ca^{2+}promoted DOC adsorption compared to Na^{+}	Singh et al. (2016, 2017a, b)

Adopted from Singh et al. (2018)

functionalities all of which restrict their degradation. It is a resistance to decomposition due to inherent chemical property of a molecule. Complex aromatic molecules that have been humified including lignin or soil organic carbon (SOC) are associated with this property. Specifically, lignin is considered to be among the plant compounds resistant to enzymatic breakdown and microbial attack since it can only be degraded co-metabolically due to its disordered and polymeric structure (Haider and Martin 1975; Hedges et al. 1985). However, it is reported that with time lignin decomposition rate is similar or even at higher rate as degradation of litter; hence selective protection of lignin seems relevant at the early stages of litter degradation (Gleixner et al. 1999; Jensen et al. 2005; Kalbitz et al. 2006; Kerem et al. 1999; Prescott 2005; Sollins et al. 2006). It is confirmed by pyrolysis and ^{13}C-CPMAS-NMR methods that lignin in the long-term is not stable and hardly stabilized in whatever soil (Baldock and Skjemstad 2000; Gleixner et al. 2002; Kiem and Kögel-Knabner 2003). Also, in plants suberans or cutans are used to produce aliphatic lipids which are strongly recalcitrant in soils (Baldock et al. 1997; Stimler et al. 2006). Evidence indicates that some compounds which accumulate in the soil are derived from microorganisms and plants including chitin, murein, certain lipids, and melanins (Guggenberger et al. 1994; Kiem and Kögel-Knabner 2003; Knicker 2004; Marseille et al. 1999). Likewise, soil microbes produce certain peptides and carbohydrates which make a significant part of the stable DOC in subsoil and appears more resistant to microbial attack (Guggenberger et al. 1994) in addition to persist in soil for several decades (Gleixner et al. 1999).

4.3 Physical Protection

Often large amount of the organic matter in soil associate with mineral colloids to make a biological resistance against decomposing organisms. In physical protection, OM form a physical barrier with the community of decomposing organisms which result in its stabilization (Elliott and Coleman 1988). The soil matrix is separated into several compartments which limit the flow of substrates, enzymes, oxygen, microorganisms, and water. The input pathways and where OM is located within the soil profile are factors to decide and determine whether microorganisms will access OM or not. The evidence for macro- and microaggregates to separate soil microorganisms and substrates is inferred by the large amount of SOM found inside the aggregates, while a significantly larger number of microorganisms reside outside of aggregates' surfaces (Golchin et al. 1994; Hattori 1988; Tan et al. 2017). Literature report the impact of soil nutrients availability on the dynamics of organic matter and community of microbial decomposers (Craine et al. 2007; Kirkby et al. 2014; Manzoni et al. 2012; Mooshammer et al. 2014). For instance, input of N in the soil potentially increase soil carbon storage resulting in subsequently lowering of microbial decomposition of SOC (Ramirez et al. 2012; Riggs et al. 2015; Zhou et al. 2014). Several mechanisms have been postulated to explain how N addition in the soil lower degradation of SOC by microbes (Riggs and Hobbie 2016). These microbial processes suggested to explain the extent N addition in the soil lower SOC mineralization includes decreased activity of ligninolytic enzyme (Eisenlord et al. 2013; Fog 1988), decreased microbial biomass (Liu and Greaver 2010; Treseder 2008), and increase in the efficiency to use microbial carbon (Ågren et al. 2001; Manzoni et al. 2012; Meena et al. 2020a). Soil organic encompasses a different functional fractions with a vast range of different biochemical composition and physicochemical protection (Lehmann and Kleber 2015; von Lützow et al. 2007). Several works propose the accessibility by microorganisms (preservation through physical and chemical processes), rather than molecular structure (biochemical/chemical composition), to determine SOC turnover rate and the way it responds toward change of the global climate (Marschner et al. 2008; Schmidt et al. 2011). Therefore, impact for N enrichment on the rate of SOC decomposition may be linked strongly to the occlusion by aggregates and mineral association (level of physicochemical protection) than with the organic substrates biochemical nature. Recently

Tan et al. (2017) examined the extent N addition in the soil affects heterogeneous responses rates of SOC degradation in various chemical and physical fraction. Results indicated that SOC turnover rate and its response to N enrichment are determined by mineral association or aggregate occlusion (the nature of physico-chemical protection) rather than to the class which the organic compound belong (biochemical nature).

5 Mechanisms of Soil Organic Carbon Adsorption in Soil Minerals

The most important mechanisms for the minerals to adsorb organic carbon in natural soil environments include (1) ligand exchange which involves covalent bonding between the hydroxyls on surface of minerals with organic functionalities (carboxyls and hydroxyls); (2) hydrophobic weak forces including van der Waals interactions and H-bonding; (3) cation mediated bridging, i.e., bridging OM by cation to negatively charged hydroxyls of clay mineral phyllosilicates and surfaces of siloxanes or oxides; and (4) electrostatic attraction (Boris and Weed 1989; Vermeer and Koopal 1998; Vermeer et al. 1998). Mikutta et al. (2007) ranked tentatively the binding mechanisms of stabilization impact in this order, ligand exchange >Ca^{2+} bridging >, van der Waals forces, based on:

(i) The mineralization which is associated to the desorption of CO_2.
(ii) Organic matter adsorbed in the presence of H_2PO_4 was most degradable.
(iii) More desorbed organic matter adsorbed in the presence of Ca^{2+}compared to organic matter adsorbed in presence of Na^+.
(iv) The mineralization was small when organic matter was adsorbed primarily through ligand exchange and larger when Ca^{2+} bridging prevailed the adsorption. These mechanisms for organic matter-clay interactions are briefly discussed hereunder.

5.1 Ligand Exchange

This strong mineral-organic matter association involves displacement of surface hydroxyl groups on minerals resulting in covalent bonding with phenolic hydroxyl groups or carboxyl groups of organic matter. The covalent bond formation in ligand exchange reactions is evidenced by the larger heat dissipated during adsorption (microcalorimetry) and the low desorption rate of OM adsorbed to Fe oxides suggesting the strongest of the bonds and reduced mineralization of OM adsorbed (Gu et al. 1994). Ligand exchange is the dominant interaction mechanism between carboxyl functionality of OM and the others on the surface of iron oxide, especially at the soil media which is acidic or slightly acidic. At low pH, the surface of Fe, Al, and Mn oxides come to be more positively charged, whereas OM come to be less negatively charged which result in interaction with organic carboxyl and OH of phenolic groups. Therefore, ligand exchange reaction is more predominant to soils in acidic media with abundance of mineral surfaces which hydroxylated sites are protonated (Shen 1999).

5.2 Cation Bridging

The association of organic matter and mineral is largely inhibited by the presence of negative charges on their surfaces. However adsorption of OM on minerals is favored by the presence of polyvalent complex. The Ca^{2+} and Mg^{2+}cations are dominant in neutral and alkaline soil media, while hydroxy polycations of Fe^{3+} and Al^{3+} are the majority in acidic media soils. Negatively charged mineral surfaces bind to these positively charged ions, and through cation bridging, long-chain negatively charged organic molecules are adsorbed (Lutzow et al. 2006; Yang et al. 2016, 2017). Varadachari et al. (1991) confirmed the increase in the preservation of non-aqueous extractable humic acid (HA) on the surfaces of the minerals such as $Al^{3+}$and Ca^{2+} in HA-montmorillonite/kaolinite/illite systems through cation bridging mechanism. Also, Ahmed et al. (2002) used citrate, EDTA, and oxalate extracts to show the extent cation bridging influence clay minerals to adsorb humus and retain it in the soil. As a result, AlfisolCa^{2+} was found not able to contribute to adsorption of humus by clay minerals via cation bridging compared to $Al^{3+}$and $Fe^{3+/2+}$. The presence of uronic acids enhance the long-chain negatively charged organic molecules to strongly adsorb to several permanent charge sites of expandable layer of clay minerals (through contact of surface segment) via polyvalent cation bridging. In many soils, cationic bridging plays significant role in the stabilization of C in which permanently negatively charged clay surfaces bind to carboxylic group (Arnarson and Keil 2000; Mikutta et al. 2007; Yang et al. 2016). Another important mechanism for OM sorption is water bridging where by polar organic functional groups bond with the hydrated shell of metals (Sutton and Sposito 2006). Cation-π interactions, a sort of the reaction involving cation bridging, also attribute to the interaction of an organic ligand through its aromatic π-electron systems with the charged siloxane surface clay mineral (Keiluweit and Kleber 2009). However cation bridging mechanisms for adsorbing OM are weaker when compared to ligand exchange interactions (Benke et al. 1999; Kaiser and Zech 2000b).

5.3 Electrostatic Attraction

Cation exchange results in electrostatic interaction of OM and the surfaces of soil mineral. Electrostatic attraction occurs on the exchange complex when the protonated amines, positively charged organic molecules, replace inorganic cations (Wang and Lee 1993). The negatively charged clays adsorb small positively charged organic compounds through cation exchange. Since the basic organic molecules carry positive charge density which strongly depends on pH, the adsorption by electrostatic attraction is a function of the basicity of the organic molecules and pH of the soil media. Preferably electrostatic attraction dominates in the stabilization of OC in acidic soils since low pH media promote the formation of positive charge on the surface of organic molecule. The bonding strength is determined by the type of cations available on the exchange sites and length of organic molecules. Bonding may also form by the penetration of organic molecules between the layers of expandable 2:1 clay mineral surfaces by means of intercalation controlled by the density charge on the surfaces, size complexity, and shape of the organic molecules (Lagaly et al. 2013; Sarkar et al. 2012).

5.4 Hydrophobic Interaction, van der Waals Force, and H-Bonding

At the mineral surfaces, the association of organic molecules and minerals may occur through other binding mechanisms which include the formation of hydrogen bond, hydrophobic, and van der Waals interactions. Attraction forces exerted within the long chain of uncharged carbon molecules results in hydrophobic interactions to occur. The van der Waals interactions occur due to bonding of OM to mineral surfaces since it operates to all molecules and results in individual atoms due to fluctuations of the dipole moment. A temporary fluctuation of electric charge density of one molecule produces a change in electric charge density of a nearby molecule. The phenomenon results in induction of dipole in both molecules since these forces can occur between nonpolar molecules or atoms. The polarization ability of the organic molecules and the surface area available for contact determine van der Waals interactions' contribution in the binding process. In the hydrogen bonding, a partial negatively charged O or N atom interacts with partially positively charged hydrogen atom. Protein molecules, uncharged polysaccharides, and extracellular enzymes establish associations via hydrogen bonds or van der Waals forces due to the available polar groups in the molecules such as hydroxyl ions (Quiquampoix et al. 1995).

6 Does Soil Mineralogy Have Any Impact on the Soil Organic Carbon Stabilization?

6.1 Phyllosilicates and Soil Organic Carbon Stabilization

The impact of stabilization mechanisms of SOC by clay minerals has been studied through monitoring the evolved CO_2, the growth of inoculum, and the remaining substrate. The mineralization of organic molecules is investigated in in vitro condition, occasionally by soil phyllosilicates and with pure minerals of geological origin suspension (Chevallier et al. 2003; Jones and Edwards 1998; Koskella and Stotzky 1997). Chenu et al. (2002) list five various mechanisms likely to operate concurrently and reduce the rate of biodegradation: (i) organic substrate sorbed is inaccessible to the extracellular enzymes of microbes; (ii) phyllosilicate exerts a direct effect of either maximizing or minimizing the activity of the microorganism; (iii) the extracellular microbial enzyme to mediate biodegradation process becomes inactivated when sorbed to clay minerals; (iv) the phyllosilicate clay minerals buffers the pH of the soil solution; and (v) the phyllosilicate clay minerals adsorb other toxic compounds or necessary nutrients and kept locked inaccessible to microorganisms.

Surveyed literature indicates that phyllosilicate clay minerals inhibit organic substrate mineralization. In the presence of phyllosilicates, some studies merely revealed that the rate of biodegradation has reduced, without characterizing substrate in the media and compare with the amount sorbed on the surface of the clay mineral (Chen et al. 2009; Jones and Edwards 1998; Magdaliniuk et al. 1995; O'Loughlin et al. 2000; Olness and Clapp 1972; Paget et al. 1992). Other investigations revealed the reduction in the rate of biodegradation to be understood quantitatively, through desorption limited mineralization (Chiellini et al. 2000; Masaphy et al. 1996; Miller and Alexander 1991; Ogram et al. 1985). Through assessment of several studies, it was demonstrated that mineralization of the adsorbed organic matter does not actually occur (Besse-Hoggan et al. 2009; Calamai et al. 2000; Chen et al. 2009; Chevallier et al. 2003; Crecchio and Stotzky 2001; Dashman and Stotzky 1986; Fiorito et al. 2008; Koskella and Stotzky 1997; Lozzi et al. 2001; Mikutta et al. 2007; Smith et al. 1992). The impact of different phyllosilicates in reducing the rate of biodegradation corresponds to greater adsorption capacity with the order kaolinite < illite < hectorite < montmorillonite (O'Loughlin et al. 2000). However, other studies report binding strength to be of extreme importance than amount of substrate adsorbed (Cai et al. 2011; Chen et al. 2009).

Several authors investigated relation between the type of clay minerals and SOC or SOC turnover rates in the clay size fractions in soils with diverse phyllosilicate mineralogy. For instance, Wattel-Koekkoek et al. (2003) studied the C protection in clay mineral-sized fractions of six soils dominated by 2:1 smectite and six dominated by 1:1 kaolinite. As a result, no difference in average C contents was observed between 2:1 and 1:1 dominated clay mineral fractions. Contrarily, the mean residence time for C was higher for 2:1 dominated clay-sized fractions (1100 vs 360 years). Nevertheless, later investigation of ten different Mozambican soils reported no difference in mean C residence time between kaolinite and smectite clay fraction-dominated soils (Wattel-Koekkoek and Buurman 2004). Hassink (1997) conducted experimental study to investigate the relation between carbon stabilization and dominant (1:1 and 2:1) clay type in the soil. As a result, it was found that the amount of C preserved was not affected by clay type. Also, Wattel-Koekkoek et al. (2001) reported no significant difference on the quantity of carbon in the clay-size fraction between kaolinite (1:1 clay type) and smectite (2:1). Six et al. (2002) expanded analysis of Hassink (1997) study on the impact of primary organo-mineral complexes in the physical protection capacity for C. Contrary to Hassink (1997) results, they found that 1:1 clay-dominated soils exhibited relatively lower C stabilization capacity compared to 2:1 clays probably due to the structural differences between them. Similar findings was reported by Saggar et al. (1996) who studied rate of mineralization of ^{14}C-labeled ryegrass in soils with different mineralogy in the field for 5 years. Results showed that for equal amount of clays, the rate of mineralization of ^{14}C-labeled ryegrass was high for the 1:1 kaolinite-dominated soil clay compared to 2:1 smectite clay. They also found the direct proportional relation between the ^{14}C remained in soil and specific surface area after 5 years of study.

Permanent negative charges in 2:1 clay soils such as montmorillonites, smectites, and vermiculites account for high CEC exhibited by these soils and probably ascribes to their high ability to protect SOC compared to 1:1 clay minerals such as kaolinites with low CEC. In addition to high CEC, 2:1 clay minerals also have small particle size leading to high SSA associated with their high sorption capacity and when placed in water expands. Contrarily, 1:1 kaolinite when in water does not swell; its particle size is larger and exhibits a relatively smaller SSA. However, Varadachari et al. (1994) found no relation between the amount of C adsorbed to clays and minerals surface area. Therefore, knowledge on the impact of soil mineralogy in stabilizing SOC is currently based on inadequate and contradictory information. Soil organic carbon sequestration by clay minerals is usually assumed to increase in the order of kaolinite < illite < smectite < allophane (Bruun et al. 2010; Lutzow et al. 2006).

6.2 Role of Fe/Al Oxides Minerals in Soil Organic Carbon Stabilization

In most acidic soils Fe/Al oxides adsorb and consequently preserve SOC than layer silicates, i.e., kaolinites and smectites (Chorover and Amistadi 2001; Kaiser and Guggenberger 2003). It is well-known that the amount of OC adsorbed by clay fractions is reduced when acidic soils has no Al/Fe oxides (Kaiser and Guggenberger 2000; Kaiser and Zech 2000b). Thus, Fe and Al oxide content determine the extent to which acidic soils protect SOC mineralization. For instance, more OC is adsorbed by $Al(OH)_3$ and goethite compared to kaolinite and illite (Kaiser and Zech 1999). Kothawala et al. (2009) reported increase of the soil samples' adsorption capacity (Qmax) as the quantity of extractable Fe and Al increases. This is probably due to clay-oxide-organic associations, as hydrous oxides attach to organic compounds and clay minerals (Ohtsubo 1989; Tombacz et al. 2004) impact the DOCs adsorbed by soils. Kahle et al. (2004) reported direct proportional relation between the amount of dithionite-extractable Fe (F_{ed}) and the DOC content adsorbed. As much as twice the amount of DOCs was adsorbed by the soil clay fractions compared to DOCs sorbed by the phyllosilicates. 122–146 mmol DOC kg^{-1} was adsorbed by soil clay fractions, while the phyllosilicates adsorbed 61–73 mmol DOC kg^{-1}. This indicates pedogenic iron oxides attributes to the improved adsorption of DOC by the soil clay fraction compared to the phyllosilicates. Likewise, Kaiser et al. (1996) studied several untreated soils of forest vegetation and found a positive correlation between the content of Fe_{ed} and sorbed DOC. Contrarily, no correlation was found by Riffaldi et al. (1998) in some untreated agricultural soils between DOCs adsorbed and content of Fe_d. Recently, Saidy et al. (2012) reported that coating illitic and smectitic clays with goethite has no impact on the stabilization of OC derived from plant residues compared to clays with no goethite added. This may be due to measurement of OC sorbed by iron oxide taken individually on phyllosilicate clays and oxides hence unable to test directly the interaction between these clay minerals (e.g., Feng et al. 2005; Meier et al. 1999; Mikutta et al. 2007). Saidy et al. (2013) measured sorption using batch equilibrium method in mixture containing plant-derived OM, clay minerals, and hydrous oxides. As a result, kaolinite coated with goethite significantly exhibited higher adsorption of DOCs three times compared to kaolinite without goethite. Kaolinite is reported to interact intensely with Fe oxides, inducing cementation effect, and promote the formation of aggregates which protect OC. The positively charged oxides-negatively charged clay mineral associations balance their charges leading to the clay particles being stabilized (Churchman et al. 1993; Favre et al. 2006). This protect OC from being attacked by microbes by induced clay flocculants which preserves it (Baldock and Skjemstad 2000).

6.3 Role of Cationic Species Released from Chemical Breakdown of Rocks in Soil Organic Carbon Stabilization

Weathering, an essential part of the carbon cycle, involves chemical breakdown of rocks which carbonates lockup CO_2 on the oceanic floor. The artificial acceleration is used to enhance weathering through supplying crushed silicate rocks to vegetated terrestrial landscapes. Silicate rock minerals such as basalt and olivine-rich dunite and harzburgite are chemically broken down to release cations such asMg^{2+} and Ca^{2+} associated with carbonates which react with bicarbonate/carbonate minerals or carbonic acid and adsorb CO_2 from the atmosphere (Hartmann et al. 2013; Köhler et al. 2010; Taylor et al. 2016). Basalt enhances the development of crops on extremely weathered acidic tropical soils through the increase of cation exchange capacity and soil alkalinity, reducing toxicity induced by Al and Mn, and inhibits the availability of phosphorus limiting plant growth. Dissolution of basalt or olivine releases the cationic species (e.g., $Ca^{2+}$and Mg^{2+}) which when a chemical supersaturation occurs may precipitate in soils as carbonate minerals (Manning and Renforth 2012; Renforth et al. 2015). Also, through cation bridging reactions, cationic species can accumulate and attract SOC at the surface of mineral particles which are no longer reactive. These cations cause the soil CEC to increase (Gillman 1980; Gillman et al. 2001), which together with base saturation improves SOC sequestration. Weathering of olivine-type rock minerals is most likely to release Al and Fe. An isotope of ^{13}C-labeled amino acid together with NanoSIMS experiment was designed to verify the capability of Al and Fe minerals to retain C (Yu et al. 2017). The incubation of^{13}C amino acid mixture for 24 h revealed Fe and Al to play a “nuclei” role and enhance to retain the added $^{13}C^-$ (Fig. 5a). The $^{13}C/^{12}C^-$ hue-saturation-intensity (HSI) image (Fig. 5b) further supported the $^{13}C^-$ retention which clearly showed the $^{13}C^-$-enriched spots to surround the colloid particles. Moreover, the arrays for the supply of $^{13}C^-$, $^{12}C^-$, $^{27}Al^{16}O^-$, and $^{56}Fe^{16}O^-$ are indicated to be comparable by line profile test.

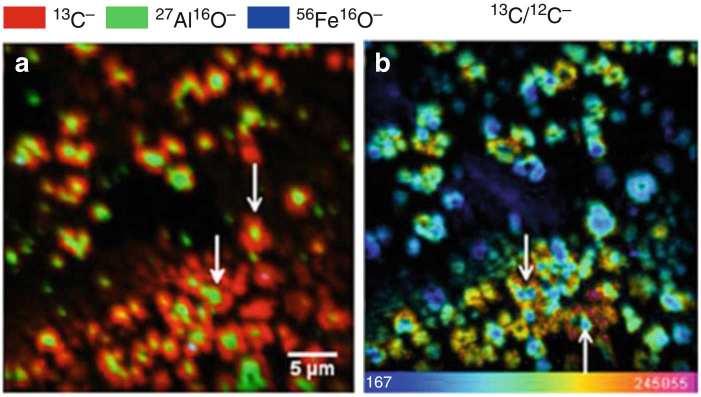

Fig. 5 Isotopic labeling experiment showing labile C retention by Al and Fe oxides. (**a**) Elemental distribution map of $^{27}Al^{16}O-$ (green), $13C^-$(red colored), and $^{56}Fe^{16}O^-$ (colored blue) after 13C-labeled amino acid incubated with soil colloids for 24 h. (**b**) Hue-saturation-intensity (HSI) images of enriched $13C^-$. (Adopted from Yu et al. 2017)

7 Warming Climate and Soil Organic Carbon Stabilization

The atmospheric change in the concentration of CO_2 affects the physical climate. In the meanwhile changes in the physical climatic condition affect the rate at which CO_2 is exchanged from atmosphere to the terrestrial soil and ocean and vice versa. With the global warming, it has become critical to evaluate impact of temperature on SOC stocks to model the feedbacks of climate-carbon cycle (Arora et al. 2013). Generally, in the atmosphere, the climate-carbon cycle parameter is positive as higher temperatures cause carbon influx into atmosphere from the terrestrial soil and ocean. The terrestrial soil and ocean capacity to fix carbon is reduced by positive climate-carbon feedback at warm temperatures resulting in the emissions of larger fraction of anthropogenic CO_2 in the atmosphere. If increasing temperature could cause SOC stocks to decrease, then in turn it could lead to positive feedback loop resulting in exacerbate global warming and increase further the concentration of greenhouse gas atmospheric CO_2. Conversely, the strategies to increase SOC stocks are potential to mitigate global warming and climate change (Chabbi et al. 2017). Comprehensive models which link the dynamics of SOC and climate tend to differ in projecting the SOC stocks fluctuations in the future (Arora et al. 2013; Friedlingstein et al. 2006). The inherent variations are relatively due to lack of certainty about the temperature sensitivity of SOM degradation, which despite large body of available literature still is a topic to debate (Davidson and Janssens 2006; Kirschbaum and Franz 2006; Lehmann and Kleber 2015; Sierra 2012). Since SOC mineralization process is a chemical phenomenon, it is mediated by microbial enzymes. Therefore, it follows Arrhenius (1889) kinetic theory, as it is temperature dependent such that rates of decomposition increases exponentially with temperature considering abundance of substrates at enzymes reaction sites. The increase in the decomposition rate is defined by the substrates activation energy, such that chemical recalcitrance of the substrates is the major issue determining proportional change in the rate of degradation per unit change in temperature (relative temperature sensitivity) (Davidson and Janssens 2006). Therefore, as chemical structure determines the stability of SOM, the kinetics theory forecasts that less stable, fast-cycling SOM would not be affected by warming compared to stable, slow-cycling SOM. This idea is empirically supported by several laboratory incubation studies as in Refs. Bracho et al. (2016), Conant et al. (2008a, b), Haddix et al. (2011), and Lefevre et al. (2014). However, several reports provides conflicting information (Fang et al. 2005; Gillabel et al. 2010; Townsend et al. 1997); therefore the controversy on relationship between temperature sensitivity and SOM stability still persists (Conant et al. 2011). SOM stability in undisturbed soil is unlikely to be fully explained by its chemical recalcitrance (Dungait et al. 2012; Kleber et al. 2011; Schmidt et al. 2011) since major portion is unavailable for enzymatic decomposition as are preserved by physical or physicochemical processes (Kögel-Knabner et al. 2008). The mechanisms for protection of SOM inside soil aggregates with limited oxygen supply are by physical isolation and partially limited to access exoenzymes and microorganisms. Chemical protection is achieved by mineral surfaces which adsorb SOM onto their surfaces through electrostatic or covalent bonds (Kögel-Knabner et al. 2008). Therefore, SOM preservation by physical-chemical means are overcome by series of reactions in the undisturbed soil environment before the occurrence of enzymatic degradation of organic substrates (Conant et al. 2011). The nature of physicochemical protection mechanisms in such circumstance may determine the temperature sensitivity of SOM rather than the nature of the substrate per se (Kleber et al. 2011; von Lützow and Kögel-Knabner 2009).

Evidence derived from laboratory experiments indicates the decomposition of preserved SOM predicted by the kinetic theory may be higher than the actual rate of degradation per unit change in temperature (temperature sensitivity) (Blagodatskaya et al. 2016; Moinet et al. 2018; Razavi et al. 2015). Nevertheless, contradictory evidences derived from field experience are observed. Moinet et al. (2018) partitioned total soil respiration into two major components, CO_2 efflux from newly released 13C-exhausted SOM and CO_2efflux from older 13C-enriched SOM. As a result between 11 and 28 °C, no increase in the rate of decomposition for SOM of the enriched pool of 13C was observed. On the other hand, Zhou et al. (2018) for 7 years took measurements monthly in a root exclusion plots and show that increasing temperature sensitivity results in increase stability of SOM (SOM increases as root exclusion plots aging). To control soil matrix on SOM turnover, the methodologies used in both studies minimized the disturbance of physical soil. However, these studies differed in the timescale with Zhou et al. (2018) using the temperature variations in the season while Moinet et al. (2018) based on diurnal temperature variations of few consecutive days to deduce the temperature sensitivity of SOM degradation. While the Earth system models are parameterized by short-term experiments through temperature responses (Friedlingstein et al. 2006; Kirschbaum and Franz 2006), the impact of warming on OC stocks is determined by other features including microbes adjusting themselves physiologically since the process takes long time (Bradford 2013; Karhu et al. 2014). Open debates are still about whether under field conditions both the long- and short-term response of SOM degradation increases temperature.

8 Conclusion

The atmospheric change in CO_2 concentration affects the physical climate which in turn affects the rate of atmospheric CO_2 exchange with the soil. Mineralization causes depletion of OC in the soil resulting in increase of CO_2 concentration in the atmosphere which in turn exacerbates global warming. Therefore, protecting SOC is crucial to mitigate climate change-related damages including global warming. Though climate change affects the whole globe, its impacts are intensely felt in some regions than others. For instance, in Africa and some parts of Asia where the major economic activities are related to agriculture, the pinch of climate change is more severe than in other regions despite contributing almost nothing in the global climate change. Currently it is uncertain, but in the future global warming may reduce soil productivity due to mineralization of OC locked in the soil which could promote plant health. Therefore, climate change mitigation should be a serious concern to save lives and makes the Earth's atmosphere a better place for life.

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Carbon Stabilisation in Tropical Ecosystem

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Abstract

Carbon (C) cycling and sequestration are two paradigms in global C stabilisation. On one part, continuous biogeochemical cycling of carbonaceous C (organic C) and C dioxide-C (CO2-C) are all vital and essential for life on the planet earth. There can be no life without C, in addition to hydrogen, oxygen and other elements known to science. The problem lies with excess CO_2-C which remains in relative gaseous phase in the environment of soil, water and air. The global limit of CO_2-C continues to rise in the era of agricultural, industrial and human civilisations that depend primarily on burning of fossil fuel, coupled with other anthropogenic activities like bush burning, deforestation, logging, gas flaring in crude oil exploration and wastes disposal. These have come with consequent environmental consequences, namely, global warming, climate change, melting of arctic ice, rise in sea level, flooding, tsunami, acidification, acid rain, desertification, pollution and habitat degradation/losses. To mitigate C excesses in the environment, scientists and researchers have tried several schemes/approaches in C sink, popularly referred to as "sequestration". The rate of sequestration in atmosphere, lithosphere and hydrosphere depends on the available methods and resources. In atmosphere, C-sequestrations have involved reforestation or afforestation to securely capture CO_2-C and store as nutrients in plant parts in the form of cellulose, hemicelluloses, starch, carbohydrate and glucose. In lithosphere, C-sequestrations have involved organic matter amendments/deposition, alley farming, silviculture and agroforestry. In hydrosphere, C-sequestrations have involved ocean fertigation with iron (Fe^{++}) fillings required by phytoplankton as nutrients. The limitation for atmospheric sink lies on global deforestation/logging for agriculture and timber, while that of lithospheric sequestration lies on high-input agriculture that makes use of inorganic fertilisers, agrochemicals and agricultural mechanisation/processing/storage that depends on burning of fossil fuel, bush burning and bush clearing for land preparation/agricultural activities. The limitation of hydrospheric sequestration lies on cost, availability and affordability of Fe^{++} fillings. Whichever method of C sink, successes and failures come with global welcome as scientists, agriculturists and researchers strive to test, develop and adapt all local, regional, national and international options, including integrated approaches/methods/formulas. The chapter "Carbon stabilisation in tropical ecosystem" is geared towards highlighting the importance of carbon sink in our ecosystem. The methods and systems of C sink or storage vary from one location to another. But the idea remains that excess gaseous carbon dioxide-C in the environment is very inimical to environmental health, and all options required for their sink and stabilisation in the environment should be accelerated all over the world to avoid what this chapter likens to "carbon holocaust".

Keywords

Carbon cycling · Carbon sequestration · Carbon stabilisation · Carbon dioxide-carbon · Human civilisations · Anthropogenic activities · Agricultural activities · Industrial activities · Environmental consequences · Burning of fossil fuel · Mitigation measures · Between nature and nurture

Abbreviations

C	Carbon
CH_4	Methane
CO_2-C	CO_2-Dioxide- CO_2
ICT	Information and Communication Technology
N	Nitrogen
N_2O-CH_4	Nitrous oxide-methane
NPP	Net primary productivity
OM	Organic matter

1 Introduction

Carbon (C) storage was described by Lal et al. (1998) as geo-engineering techniques for long-term storage of carbon dioxide (CO_2) and other forms of C desirable for the mitigation of global warming. CO_2 is normally trapped from the atmosphere via biological, chemical, or physical processes and converted during photosynthesis to harmless forms in form of hemicelluloses, cellulose, starch, carbohydrates and other end products.

According to Paustian et al. (2000), C accumulates in the atmosphere at a rate of 3.5 gigatonnes per annum, with the greatest contributor being burning of fossil fuel and conversion of tropical forests into agriculture. C storage has been proposed as a panacea to excess greenhouse gases in the atmosphere. According to Hamilton et al. (2002) and Keutgen and Chen (2001), agriculture and forestry are important in reducing greenhouse gases. This is through the storage of C in perennial vegetation and transformation of C to organic matter (West and Post 2002; Meena et al. 2020). For C to be converted to organic matter, there must be noble practices that add more C to the soil and slow down the rate that C is being converted to gaseous C dioxide.

To achieve desired purpose, it is proposed that terrestrial C storage should integrate planting of trees and crops to capture CO_2 from the atmosphere through photosynthesis and storing in biomass of tree trunks, branches, roots, fruits, forages and the soil through microbial decomposition of plant litter to generate humus and nutrients required for plant growth (Keutgen and Chen 2001). For example, Hamilton et al. (2002) estimate that 50% of the C absorbed from the atmosphere are normally used for plant growth, while the remaining 50% are used for photosynthesis and plant litter.

Hence, the advocacy has been on management practices vital for C storage and which will also conform to global principles of sustainable agriculture. According to Paul et al. (1997), they range from reduced tillage, erosion control, diversified cropping systems and improved soil fertility.

2 Carbon Dynamics: Empirical Sciences

C-cycle is driven by soil microorganisms which regulates C and energy flow in the system (RCEP 1996). The major source and sink for greenhouse gases has been in the soil. The amount of C in decaying plant litter and soil organic matter has been estimated to exceed the ones in living biomass by a factor of 2 or 3 (RCEP 1996).

C has been found to accumulate in soil when arable land is used for grassland or forest, while it takes ten times longer to build C when arable land is converted to pasture than it takes to deplete C stocks after pasture has been converted to arable land (RCEP 1996). The RCEP (1996) reports that accumulation of C is much slower when arable land is moved to pasture, where around 49 t C ha^{-1} may be added in over 275 years, with half of this amount in the first 38 years.

Human influence on the natural cycle has been attributed to accelerated release of CO_2 to the atmosphere (Cannel et al. 1994). To capture and store these C that would otherwise be emitted to the atmosphere (FAO 2000; Pretty and Ball 2001), scientists have recommended replacement of CO_2-producing energy sources with cleaner fuels, followed by ecological sinks for atmospheric sinks for atmospheric CO_2 (Lackner 2003; Meena and Lal 2018; Ogunseitan 2005). This is possible due to the role of microorganisms in C sink in both terrestrial and marine ecosystem (Lackner 2003).

The accumulation and turnover of soil organic matter has been a major factor in soil fertility and ecosystem stability. It also determines when soils act as sink or sources of C in global C pool (Post and Kwon 2000; Paul et al. 2003). Soil organic matter dynamics involve diverse organic constituents (Sollins et al. 1999) with various mean residence time. Field evidence for C sink in soils varies from place to place. In some cases conversion of forest or grassland to agriculture has been proved to cause losses in C (Mann 1986; Post and Kwon 2000). This was found to re-accumulate if the arable land was restored to native vegetation, while in other instances, large re-accumulations of C in soils have been observed following conversion of arable lands to forests. In other cases, little or no re-accumulation (Compton et al. 1998; Richter et al. 1999; Compton and Boone 2000), while Post and Kwon (2000) discovered large variations in agricultural abandonment (both negative and positive), while Schlesinger (1990) recorded 0.33–0.34 Mg C ha^{-1} y^{-1}(Pretty and Ball 2001), demonstrated that sustainable agricultural systems can accumulate 0.3–0.6 t ha^{-1} when trees are intercropped in cropping and grazing systems. Johnson and Curtis (2001) found that forest harvesting followed by reforestation can accumulate little or none. Farage et al. (2005) observed different scenarios in Nigeria, India, Kenya and Argentina. The systems in these localities recorded various amounts during tillage. Farage et al. (2005) reported that addition of organic matter to the soil with farmyard manures, green manures, legumes in rotations, vermicompost or fallows-in-rotations increased soil C and trees as part of agroforestry systems further increased C stocks. On the other hand, the use of organic fertilisers resulted in the decline in soil C in all systems or small increments when used with zero tillage, while zero tillage increased C accumulation especially following addition of organic matter to the soil (Farage et al. 2005).

2.1 Carbon Tinkering in the Soil: The Role of Biota

Microorganisms are the earth's most versatile inhabitants and can withstand harsh environmental conditions (Ogunseitan 2005). Microorganisms colonise land, sea and air, either as free living or as parasites or in symbiosis with other organisms. One gram of soil may contain billions of microorganisms including bacteria, fungi, protozoa and algae (Ogunseitan 2005). Microbial population plays a key role in sanitizing the planet earth, fixing atmospheric gases and degradation of organic matter. Without them there would be no life on the planet (Ogunseitan 2005).

Soil microorganisms are vital in determining the pattern of associations in geochemical cycles. Their role in cycling of C and N is very prominent. Soil is one of the most diverse habitats on earth and contains numerous organisms. The soil microorganisms are mainly responsible for biological activities of the soil (over 60–80%) and govern nutrient cycles in the soil (Baskin 1997; Bardgett 2005).

Earthworms often form a major part of the soil fauna and represent nearly 50% of the soil biota, especially in some temperate grasslands and up to 60% in some temperate forests (Bardgett 2005). The complexity of bacteria, fungi, actinomycetes, viruses and nematode interactions in the soil food web regulates nutrients and energy flow in the soil (Oades 1993). Figure 1 shows a typical soil biodiversity (Hillel 2008).

The soil bacteria are highest in number as one gram of soil can contain up to one billion bacterial cells and over 10,000 bacterial genomes (Bardgett 2005). Despite the small size of bacteria (less than 2μm), they constitute 3–5% of the total soil organic matter content (Oades 1993), while new species and genera are continuously being discovered (Baskin 1997).

The metabolic pathways of soil microorganisms are unique. Some decompose cellulose or persistent organic compounds in or absence of oxygen (Bardgett 2005). Bacteria are responsible for decomposition of over 90% of the total soil organic matter. The by-products of this decomposition are water, C dioxide and energy (Baskin 1997).

Fungi are diverse group, and one gram of soil can contain over one million organisms. In temperate soils, fungal biomass exceeds bacterial biomass by a factor of 2 and can amount to 2–5 t ha^{-1}(Baskin 1997). Soil algae are similar to plants and require light as source of energy. Hence, algae only inhabit few millimetres of the top soil, and they are dependent on soil nutrients (Oades 1993). Protozoans are the smallest of soil animals and comprise various taxa, e.g. amoeba, flagellates and

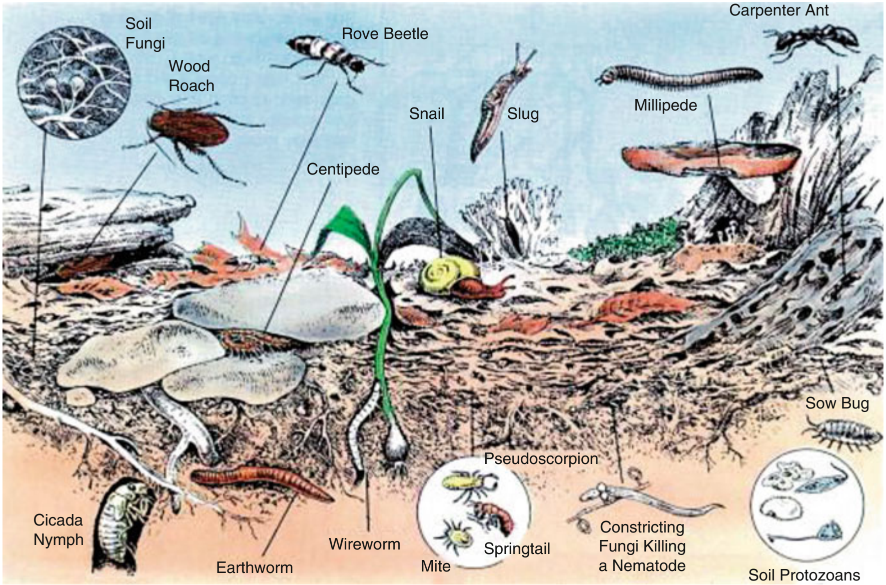

Fig. 1 Soil organisms (Hillel 2008)

ciliates. They require oxygen for respiration. Protozoan feed primarily on bacteria, and some use organic matter as source of energy (Bardgett 2005).

Nematodes are tiny non-segmented worms with uniform morphological features. They can reach densities of 10–50 individuals per gram of soil. Many feed on bacteria, whereas others live as parasites of plants (Baskin 1997). Earthworms make up over 3000 kg ha^{-1} of soil and make up major populations of agricultural soils. The pot worms are relatives of earthworms, and densities range from 10^2 to 10^6 m^{-2} (Bardgett 2005).

Microorganisms are chemical engineers of the soil (Bardgett 2005) and responsible for cycling of nutrients especially C and N (Ogunseitan 2005; Meena et al. 2018). In view of place of soil and soil biota, the United Nations declared 2015 as the International Year of Soil. The first status of the World's Soil Report was published at the end of 2015. The first Global Soil Biota Atlas was published in 2016 (Eisenhauer et al. 2007). Though these projections work, the understanding and recognition of role of soil and biota on the future of all life on earth continue unabated (FAO 2015).

2.2 Carbon Losses and Gains in Dynamic Ecosystem: Any Hope for Equilibrium Science (Equoscience)

C and nitrogen are the building block of soil organic matter (Janzen 2006), while majority of C in agricultural system arises from photosynthesis. Plants either respire or use C in the production of organic compound (Vitousek et al. 1997). The C-containing compounds harvested with the plants are added to soil as aboveground biomass or belowground biomass (Janzen 2006). Soil microbes respire a high level of C, while the remaining is humidified to soil organic matter (Janzen 2006). The author reports that accumulation of soil organic matter occurs when the amount of C added via biomass exceeds the rate of soil organic matter decomposition.

The amount of soil organic matter determines the soil health and capability to recycle nutrients in the ecosystem. They can be lost in the course of soil tillage (Peterson and Vetter 1971). The organic matter of the soil acts as its sources or sink. When organic matter is added to the soil (Janzen et al. 1997), reports that the net remains in the soil in absence of any threat from erosion will be the balance arising from the ones supplied via the residues and the ones lost in course of soil microbial respiration. When the remains of plants and animals are returned to the soil, the level of soil organic matter improves (Campbell et al. 2000a, b). The continuous putting of a soil under fallow has been found to remove soil organic matter faster than when organic matter is continuously added to the soil (Campbell et al. 1990; Larney et al. 1997).

In most of the studies conducted in US Great Plains (Peterson et al. 1998), it was reported that continuous cropping, especially when combined with reduced tillage, was effective in adding organic wastes to the soil and simultaneously increased the level of soil C stored in the soil, while Nyborg et al. (1995), Peterson et al. (1998) and Campbell et al. (2000a, b) found that continuous cropping raised soil C in the tissues of plants growing on the surface of soil and the parts growing beneath the soil, especially when fallow system is avoided. This led to more soil organic matter. Wienhold and Halvorson (1999) also reported more soil C under continuous annual cropping compared to continuous crop-fallow system in their continuous cropping history of 11 years, while Campbell et al. (1991) saw the decrease in soil C by 5.1% when soil was continuously cropped compared to when corn was planted in rotation of wheat which gave 7.2% C reduction.

All values are expressed in units of Mg C ha^{-1} (C stocks) or Mg C ha^{-1} year^{-1} (C flows), rounded to whole numbers to emphasise high uncertainty. The estimate of net primary productivity (NPP) is based on Goudriaan et al. (2001). The rate of residue input includes both direct additions, as plant litter, and indirect additions (e.g. animal manure) and assumes, for this illustration, that net export amounts to one-third of photosynthetically fixed C, though this value is uncertain (Ajtay et al. 1979; Goudriaan et al. 2001; Meena et al. 2020b; Saugier et al. 2001; Smil 2002).

Figure 2 illustrates a typical C losses and gains in the ecosystem (Janzen 2005). However, the differences in soil organic matter lie on the original soil organic matter level, as seen in a thick Black Chernozem soil at Melfort, SK, which had high soil organic level of 61–67 t ha^{-1} (Campbell et al. 1991) and whose level remained nearly the same, even after crop rotation and addition of fertilisers. According to the scientists, it is difficult to experience increases in soil organic matter in a soil that is already high in organic matter irrespective of the type of soil management practices. This finding was compared to the ones of Campbell and Zentner (1993) in drier, Brown Chernozem soil at Swift Current, SK (Campbell et al. 1991), where soil

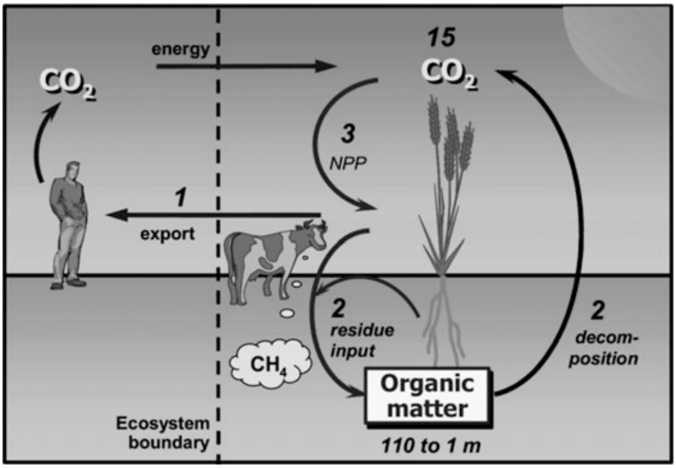

Fig. 2 An illustration of pools and flows of carbon in agroecosystems, corresponding roughly to average values for the world's croplands

organic matter increased with continuous cropping rotations and fertiliser applications. In fact, in those findings the level of increases in soil organic C was dependent on soil water content, soil initial fertility, the amounts of fertilisers applied and the period of soil management (Peterson et al. 1998). For the scientists, they believe that maintenance of soil organic matter must be achieved by adequate nitrogen management by intercropping with legumes capable of nitrogen fixation or by continuous addition of organic materials to balance the amount removed by the crops, as well as lost by erosion (Grant et al. 2002). Therefore, C losses and gains are difficult to balance and quantify and, hence, long task for advocates of equoscience. The rates of losses are sometimes greater than gains, especially in fragile tropical ecosystem.

3 Carbon Sink

3.1 Between Conservation and Conventional Tillage Systems

The Soil Conservation Society of America – SCSA – (1982) defined soil conservation as part of land conservation involving the protection, improvement and the use of natural resources according to principles that will assure the highest economic use now and in the future. This implies that each piece of land should be used *in* accordance with its capability and limitation (Babalola 2000). This, indeed, is the most cardinal principle of soil management and soil conservation.

The most significant process of soil degradation is soil erosion by water and wind and subsequent losses of water and plant nutrients through runoff water and wind drag net (Babalola 2000). Soil degradation is so closely connected with soil erosion

Fig. 3 Soybeans grown into corn stalks in a no-till field in Union County, Iowa (USDA) (Plumer 2013)

that the two terms can be used interchangeably (Babalola 2000). Many farmers in the tropics are faced with soil conservation problems. The problem of soil conservation arise from improper bush clearing, poor tillage practices, bush burning, soil exposure, marginal lands, fertiliser use, mono-cropping and over-exploitation (Babalola and Zagal 1999; Nnabude 1999; Babalola 2000). Figure 3 shows a typical no-till farm system (Plumer 2013).

Many soil management and soil conservation measures have been suggested (Babalola 2000). These include appropriate land use practices, adoption of well-tested soil conservation measures, soil testing for fertiliser application and desertification control.

Land use plan should indeed be the beginning of soil conservation. Appropriate land use practices require that the best soils be used for crop production and the steep slopes be not cultivated at all but put into permanent forests or pastures (Babalola 2000). Land use patterns should be based on knowledge of soil types to which they are put into use, choice of crops, the land improvement works required and erosion control measures. This requires a detailed Soil Map complete with land capability and suitability classification of the soils for different uses in each region of the world (Babalola 2000).

The primary aim of soil conservation is to introduce and encourage a stable system of land use and management which controls and prevent erosion by protecting the surface of the soil from direct rainfall impact, ensuring that the maximum amount of water reaching the soil surface is absorbed by the soil, adopting practices that will safely dispose runoff from the field (Babalola 2000). These can be achieved through biological or agronomic measures and physical or mechanical measures (Babalola 2000). Soil conservation plan for any ecological belt combines both measures.

Continuous soil testing and recommendations for fertiliser application has been advocated for sustainable agricultural production and soil conservation (Babalola

2000). Fertiliser application by peasant farmers in the tropics is largely based on generalised fertiliser recommendations which are not always appropriate. Hence, appropriate practice will not only boost crop production, but will also help to minimise possible negative effect of pollution and adverse effect on biotic life that may be triggered by high dosage of fertiliser (Babalola 2000).

Some of the well-tested and established conservation practices to combat wind erosion such as cultivation to produce rough surface and surface ridging for loose soils are not yet routine practices in most parts of the tropics (Babalola 2000). The problem of desertification can be controlled by afforestation programmes, establishment of grazing and browsing reserves, establishment of wind breaks, shelter belts construction, sand dune stabilisation, alternative sources of energy for cooking to remove pressure on wood energy and a comprehensive land use planning (Sagua et al. 1985). Although the permanent stabilisation of sand dunes is best done by establishing a permanent vegetation on the dune, the problem should not be looked as a routine afforestation (Babalola 2000). This is because vegetation will not grow where there is active dune sand movement. Appropriate dune stabilisation requires that drought-tolerant and fast-growing plants be used and that mechanical defences be installed for the seedlings in order to prevent them from being buried (Babalola 2000). Such defence should be in a check-hazard arrangement to take care of fluctuating wind directions. Such a technology as developed by Babalola (1998) needs to be continuously tested and validated on large scale basis on dunes.

Techniques which in literature are known as reduced, minimum and zero tillage are soil conservation practices in the tropics (Oparaugo 1994). Zero tillage refers to a system that eliminates all pre-planting mechanical seedbed preparation except for the opening of a narrow strip (2–3 cm wide) or hole in the ground for seed placement to ensure adequate seed/soil contact (Oparaugo 1994). The entire soil surface is covered by crop residues. Limited tillage is especially relevant where tillage could have negative effects by forming a crust on the cultivated soil (NALDA 1994; Oparaugo 1994) and thereby increasing erosion or where the soil is difficult to work. This technique can be combined with strip cropping and terracing (NALDA 1994).

Omebe (2019) observed soil organic C of 25.9 g kg^{-1} in zero tillage + herbicide; 23.0 g kg^{-1} in zero tillage + manual weeding; 27.1 g kg^{-1} in ploughing only; 19.0 g kg^{-1} in ploughing + harrowing once; and 31.5 g kg^{-} ^{1}in ploughing + harrowing twice in an ultisol in Abakaliki, Southeastern, Nigeria. Agbede (2006) supported the capability of an Alfisol of Southwestern Nigeria to store C under adequate tillage and other management system, while Chang and Lindwall (1989) supported effect of long-term minimum tillage practices on some physical properties of a chernozemic clay loam. Derpsch et al. (2010) detailed the status of adoption of no-till farming in the world, and their main benefits included soil C restoration.

Fabrizzi et al. (2005) listed soil water dynamics, physical properties that command wheat responses to minimum and no tillage systems in Southeastern Pampas of Argentina. Gürsoy et al. (2011) explored effects of ridge and conventional tillage systems on soil properties and cotton growth, while Husnjak et al. (2002) described effect of different tillage practice systems on soil physical properties and crop yield.

Similarly, Iqbal et al. (2005) studied effect of tillage and farm manure on some soil physical properties and growth of wheat (*Triticum aestivum* L.), and Jabro et al. (2009) discussed tillage effects on physical properties in two soils of the Northern Great Plains. Kabir et al. (2013) enumerated effect of mulching and tillage practices on soil penetration resistance and crop growth. On the other hand, Khurshid et al. (2014) described effect of tillage and mulch on soil physical properties and growth of maize. Other authors (Lipiec et al. 2006; Rashidi and Keshavarzpour 2007; Moreno et al. 2008; Mosaddeghi et al. 2009; López-Garrido et al. 2012) explained tillage system on soil health including C storage.

Ikechukwu (2016) who studied effect of tillage practices and wood ash on soil properties and response of castor (*Ricinus communis*) on an ultisol in Abakaliki, Southeastern Nigeria, recorded 7.70 kg^{-1} C in mound without wood ash; 9.70 g kg^{-1} C in mound +2 t ha^{-1} wood ash; 12.10 g kg^{-1} C in mound +4 t ha^{-1} wood ash; and 11.30 g kg^{-1} C in mound +6 t ha^{-1} wood ash during the year of cropping. During the second year, 8.10, 6.10, 6.50 and 6.90 g kg^{-1} C was observed in the respective treatments. In the third year of cropping, 7.20, 19.8, 16.4 and 17.4 g kg^{-1} C was recorded in the respective plots. Similarly, the same author recorded 0.56 g kg^{-1} C under ridge without wood ash; 10.9 g kg^{-1} C in ridge +2 t ha^{-1} wood ash; 12.90 g kg^{-1} C in ridge +4 t ha^{-1} wood ash; and 10.1 g kg^{-1} C in ridge +6 t ha^{-1} wood ash during the first year of cropping. During the second year of cropping, 8.50, 13.0, 9.30 and 9.70 g kg^{-1} C was observed in respective treatments, while 12.0, 18.3; 16.9 and 17.4 g kg^{-1} C was recorded in respective plots during the third year of cropping. Then in flat tillage system without wood ash, Ikechukwu (2016) observed 10.9 g kg^{-1} C; 3.9 g kg^{-1} C in flat +2 t ha$^{- 1}$ wood ash; 6.10 g kg^{-1} C in flat +4 t ha^{-1} wood ash; and7.2 g kg^{-1} C in flat +6 t ha^{-1} wood ash during the first year of cropping. During the second year of cropping 14.5, 9.3, 13.3 and 6.3 g kg^{-1} C was observed in respective treatments, while 18.0; 13.0, 15.4 and 17.8 g kg^{-1} C was observed in respective plots during the third year of cropping. There were no significant differences in tillage method and rates of wood ash application, but significant differences in tillage and rates of wood ash application in Ikechukwu (2016) studies. All these substantiate the fact of tillage and land management practices on C storage in the tropics.

3.2 Between Crops and Cropping Systems

The tropical ecosystem is endowed with diverse plant species (Agboola 2000). The diversity of multi-cropping pattern has been observed to decline poleward or as the altitude increases within the tropics and as rainfall amount decreases (Agboola 2000). The floral composition is often in equilibrium with the environment by their interactive effects. Thus, there is a stability in the ecosystem and natural hazards like erosion, and swift mineralisation is reduced to the barest minimum (Agboola 2000).

In a typical natural tropical environment particularly in the forest zone, diverse plant species are found growing at different heights forming canopy strata, some at

Fig. 4 Teaching and research advances at Ebonyi State University, Abakaliki, Nigeria. Department of Soil Science and Environmental Management, Faculty of Agriculture and Natural Resources Management. Farming system researches in maize (*Zea mays*) (Igboji 2019)

lower layers. Thus, diversity in growth habit makes the different flora species utilise varied levels of solar radiation (Agboola 2000). Those at the lower strata are able to synthesise food at low radiance. Therefore, multi-storey cropping system is commonly practised and tends to mimic the natural ecosystem by having different crops in mixtures and varied canopy strata (Agboola 2000).

Natural multi-storey stabilises the environment and protects it from hazards like high rainfall intensity which culminates in erosion, loss of nutrients, and high temperature which leads to high rate of mineralisation (Agboola 2000). A special feature of plantains, some shrubs and most tree crops is their being amenable to multi-storey system (Agboola 2000). The planting of crops with different architectural background gives opportunity for efficient tapping of sunlight energy, mineral nutrients and soil moisture (Ruthanberg 1980).

Figures 4 and 5 are excerpts of teaching and research advances in farming system at Ebonyi State University, Abakaliki, Nigeria, Department of Soil Science and Environmental Management, Faculty of Agriculture and Natural Resources

Fig. 5 Teaching and research advances at Ebonyi State University, Abakaliki, Nigeria, Department of Soil Science and Environmental Management, Faculty of Agriculture and Natural Resources Management. Farming system researches in groundnut (*Arachis hypogea*) and *Amaranthus hybridus* (Igboji 2019)

Management. Farming system researches in maize (*Zea mays*), *Arachis hypogea* and *Amaranthus hybridus* (Igboji 2019).

In plantations, occasionally there are two-storey cropping where two perennial crops, e.g. rubber and cocoa, are inter-planted. In Nigeria, under arable cropping in the humid forest zones, ground cover is provided by sweet potato, cowpea, melon, pumpkin, gourd and calabash, while cassava, maize and yam form the middle strata, while banana, plantain and papaya which rise above the rest of the crop provide the canopy (Agboola 2000). Where maize is planted, it provides a trellis for beans that enrich the soil with nitrogen, while the live mulch crops provide ground cover, thereby reducing soil erosion, soil compaction and weed growth (Agboola 2000).

In tropical Nigeria, compound farms are intensively managed, and it has been observed that they protect the soils better and occurrence in these farms is limited (Agboola 2000). Farmyard manure in the form of poultry droppings and animal wastes as well as household refuse is used to maintain soil fertility.

The tree crops grown in compound farms are citrus species, mango, plantain, banana, guava and cashew; shrubs planted are bitter leaf and medicinal herbs. Arable crops include cocoyam, maize, sweet potato and any plant needed by the farmers family (Agboola 2000). These are sources of food and income for rural women. Animals such as goats and sheep are also kept and are fed with leftover foods, but precautions are taken to keep them off the cultivated area (Agboola 2000).

In southern Nigeria, which is one of the most densely populated part of Africa, the farmers have developed a more sophisticated system of trees and arable crop farming systems that mimic natures' multi-storey vegetation as in the rainforest (Agboola 2000). The components of the mixture, which are not systematically arranged, allow trees that are scattered at random within the farm but spaced wide enough for arable crops to be introduced (Agboola 2000).

The farmers permit high overhead tall trees such as oil palm (*Elaeis guineensis*) and coconut (*Cocos nucifera*) to exist along with medium trees such as African breadfruit (*Treculia africana*), native pear (*Dacryodes edulis*), raffia palm (*Raphia hookeri*) and *R. vinifera* followed by layer of shorter trees like kola nut (*Cola nitida*) or oranges (citrus species) and pawpaw (*Carica papaya*), banana and plantain (*Musa* spp.), yams (*Dioscorea* spp.) whose vines climb 3–6 m tall, pruned *Acioa barteri*, cassava (*Manihot esculenta*), maize (*Zea mays*) and okra (*Abelmoschus esculentus*); bush reach shoulder high, while cocoyam (*Colocasia antiquorum*) and *Xanthosoma sagittifolium* and pepper (*Capsicum frutescens*) form the next horizon (Agboola 2000). Finally, crop like egusi (*Citrullus colocynthis*) and vegetables form the lowest layer (Agboola 2000).

Economic tree stands are pruned as the need arises to reduce its shading effect on lower-growing plants. This farming practice tries to exploit the differences in natural and variable resources such as soil, water, food and labour availability all the year round with minimum exposure of the soil to harsh weather conditions (Agboola 2000). This is the case of cropping system in typical Nigerian ecosystem as applicable to other parts of the tropics.

Chigbo (2017) studied the effect of legume-cereal intercropping on plant productivity and soil C and nitrogen sequestration in Abakaliki, Southeastern Nigeria. In this work initial soil C was 11.7 g kg^{-1}. After cropping, 12.5 g kg^{-1} C was recorded under sole maize, 12.4 g kg^{-1} C under green gram; 12.7 g kg^{-1} C under black gram; 13.5 g kg^{-1} C under maize + green gram intercrop; 14.2 g kg^{-1} C under maize + black gram intercrop; 12.5 g kg^{-1} C across sole crop combinations; and 13.9 g kg^{-1} C across intercrop combinations. Cong et al. (2014) reported soil C to be higher by 4% in intercrop and sole cropping systems of 184 ± 60 kg C ha^{-1} y^{-1}. Similarly, Bichel (2013) observed maize-soybean-based intercropping systems' greater potential for C storage than conventional cropping. In that work 2 rows of maize +3 rows of soybean was recommended for optimum C storage.

Slater (2015) studied the influence of legume cropping sequences on aboveground and belowground C and nitrogen inputs in pulse-crop rotations, while Udu (2019) studies on C storage under different gmelina forest, and already cultivated farmland 25.5 g kg^{-1} C was observed in Odomoke cultivated soil, 27.1 g kg^{-1} in Azugwu gmelina forest and 19.0 g kg^{-1} C in continuously cultivated arable land. Franzluebbers et al. (2000), Blanco-Canqui et al. (2013) and Jinbo et al. (2007) reported stratification of soil C with depth in many ecosystem managed grasslands, forests and conservation-tilled cropland. According to the scientist's stratification of soil, C occurs with time when soils remain undisturbed from tillage, e.g. with conservation tillage and pastures and sufficient organic matter addition to the soil with cover crops, sod rotations and diversified cropping systems.

3.3 The Alley Farming Systems

Alley cropping is a cropping system in which food crops are planted in the alley of inter-row spaces formed by the shrubs and food crops (Agboola 2000). The shrubs are normally planted as hedgerows which are cut back at cropping time and kept pruned all through the period of crop growth to preclude shading and minimise competition with food crops (Agboola 2000). Continuous soil loss by runoff maintains soil moisture and provides an environment that favours micro- and macro organisms and soil fauna and suppress weeds (Agboola 2000). The pruning also enables nitrogen and other elements to be recycled and is used as fodder for livestock, staking material and fuel wood (Agboola 2000).

Alley cropping has common features with the traditional farming systems. During the 3–4 years in which the land is intensively cultivated after fallow, farmers practice a rudimentary form of alley cropping (Agboola 2000). In southern Nigeria, arable crops are planted between scattered fruit trees like mango, cashew and oranges. In the savannah and semi-arid zones of Northern Nigeria, shear butter, *Parkin* spp. and *Acacia albida* are left scattered on the field (Agboola 2000). The traditional alley differs in their layout. Alley cropping is organised as straight rows or alleys. The traditional farming system minimises erosion that is aggravated under mono-culture with open, clean and clear cultivation (Agboola 2000).

Alley farming/cropping has not been acceptable to farmers in rural Nigeria, but it has been used in different ways. In Ayepe it has been used by farmers in their "snairy project". Some farmers use the poles for fencing, rooting and firewood in palm oil processing. Some farmers grow economic trees like oil palm in the midst of alley trees such as leucaena and gliricidia and local trees like "iroko" and "mahogany". The alley crops supply nutrients such as nitrogen, since leucaena and gliricidia are nitrogen fixers, while the economic trees supply palm oil and kernel; the iroko and mahogany supply fodder for livestock and stakes for other tuber crops like yam (Agboola 2000).

Farmers in Nigeria reject the idea of straight rows but use *Gliricidia sepium* cut and carry for their animals. In essence, alley farming/cropping has not been totally rejected by local farmers in Nigeria. It has not been tried on sloppy lands (Agboola 2000). Figure 6 presents a typical alley cropping system (Association for Temperate Agroforestry 2019).

Ignatius (2017) who studied effect of six different hedgerow trees of alley cropping system as a C sequestration option for agricultural land in Abakaliki, Southeastern Nigeria recorded 91.0 g kg^{-1} C under alley; 173 g kg^{-1} C under *Azadirachta indica* alley; 101 g kg^{-1} C under *Acio bateri* alley; 167 g kg^{-1} C under *Adansonia digitata* alley; 204.3 g kg^{-1} under *Leucaena leucocephala* alley; 202 g kg^{-1} C under *Gliricidia sepium* alley; and 155.3 g kg^{-1} C under *Gmelina arborea* alley for first year of studies, during the second year, 94, 182, 122, 287, 309.2, 201 and 188 g kg^{-1} C for respective alley and for third year 96, 212, 167, 262, 240 and 172 g kg^{-1} C for respective alley systems.

Fig. 6 Alley cropping. (Adapted (Association for Temperate Agroforestry 2019))

Mbah and Idike (2011) worked on C storage in tropical agricultural soils of southeaster Nigeria under different management practices while assessing soil organic C dynamics, functions and management.

3.4 The Agroforestry Systems

Cultivated trees and agricultural crops in close association with one another is an ancient practice throughout the world. Tracing the history of agrofrestry in Europe (King 1987) described the practice as being old as the Middle Ages, where the general custom was to clear degraded forest, burn the slashes, cultivate food crops for varying periods on the cleared area and plant or sow trees, before, along with, or after sowing agricultural crops. Although this farming system is no longer popular in Europe (King 1987), it is still being practised in most countries of the world like Finland up to end of the twentieth century and in Germany up to the late 1920s (King 1987).

In tropical America, many farmers have practised the system (Wilken 1976). For example, in Central America, where farmers plant many species of plants on plots as large as one hectare or where coconut, papaya, bananas or citrus, coffee, cacao, maize and squash feature on farmers' fields, each with unique structure and configuration (Wilken 1976).

In Asia, the Hanunoo of the Philippines practice a unique shifting cultivation of clearing the forest for agricultural use and deliberately spare certain trees, which provides canopy to rice, thereby preventing excess exposure of rice to sun rays (Wilken 1976). Trees are part of Hanunoo farming system, either planted or preserved from original forest to provide food, medicine, wood and cosmetics. Similar practices abound in many parts of tropical Asia.

Fig. 7 Agroforestry – Integrated Agriculture. (Adapted (Instructables Living 2019))

In tropical Nigeria Agboola (2000) gave a breakdown of how common crops like yams, maize, pumpkins and beans are grown along with scattered trees. In the Yoruba of western Nigeria with history of intensive system of herbs, shrubs and tree crops, it is an inexpensive way of maintaining soil fertility, controlling leaching and erosion (Agboola 2000). Figure 7 shows a typical agroforestry system (Instructables Living 2019).

These innumerable examples of traditional land use practices involving production of trees and agricultural crops on the same piece of land in many parts of the world is what is known as "agroforestry" (Anderson and Sinclair 1993; Agboola 2000; Otegbeye 2002). There are many types of agroforestry systems: trees on farmland, parkland, alley cropping, wind breaks and shelter belts (Okali and Sumberg 1985). The method for farmland involves in situ retention of trees/shrubs during land preparation or bush clearing. In protected parklands, there is system of using trees and flowers to beautify the environment, in order to raise the aesthetic value and invariably act as carbon sink. The alley system involves using of nitrogen fixing plants in between rows of crops to act as both source of nutrients, fodders for livestock and ecosystem stabilisation (which invariably sinks C). The trees used for shelter belts are deep rooting ones capable of tapping nutrients beyond the soil horizon. They are also capable of wind breaks and checking desertification. In addition to these benefits, C are stored leading to C stabilisation in the soil (Okali and Sumberg 1985). Many wind break trees include neem (*Azadirachta indica*), gmelina, mahogany, eucalyptus and many exotic species. This is a natural resource management of integration of trees on farmlands and agricultural terrain (Leakey 1996). Agroforestry is typical of the "taungya" system in environmental, social, economic, plant species, arrangement and management (Leakey 1996).

A mature poplar tree has been reported to sequester 266 kg C, while green ash sequester 63 kg C; white spruce, 143 kg C; and caragana tree, 39 kg C (Kang et al. 1990; Anderson and Sinclair 1993; Hayashi et al. 1995; Alao and Shuaibu 2011).

According to Anderson and Sinclair (1993) at a recommended spacing for shelter belts, these trees C sequestration values translate into 106 t km^{-1} for poplar, 25 t km^{-1} for green ash, 4 t km^{-1} for white spruce and 26 t km^{-1} for caragana. These figures do not include the amount of C that will be sequestered in trees roots, up to 50–75% of C stored aboveground (Kang et al. 1990). Other works have focused on the rates at which C is accumulated in tree and shrub species. Poplar trees grow quickly and accumulate C at a faster rate. Slower-growing species, such as spruce, accumulate C at a slower rate. Slower-growing trees live longer and work as C sinks for longer periods of time and allows experts to predict the C sinks for respective agroforestry systems (Kang et al. 1990).

3.5 The Silviculture Systems

Silviculture is the art and science of controlling the establishment, growth, composition, health and quality of forests and woodlands to meet the diverse needs and values of landowners and society such as wildlife habitat, timber, water resources, restoration and recreation on a sustainable basis (Alene et al. 2008). This is accomplished by applying different types of treatments, namely, thinning, harvesting, planting, pruning, prescribed burning and preparation (Henao and Baanante 1999).

Agrosilviculture is invariably called the "taungya" methodology used to maintain forest reserve (Nwoboshi 1982). It comprises the use of arable and tree crops, with particular interest in the arable crops required for sustainable agriculture and human development. It is similar to shifting cultivation (Nwoboshi 1982), with economic trees inter-planted with grassland or forests which can mature at the same time. Silvo-pastoral schemes integrate animal production with beneficial trees. It is very useful in rearing of livestock and production of economic trees very essential in farm diversity and income/food security (Nwoboshi 1982).

Adekunle et al. (2013) and Sarah (2015) classified silviculture to C sequestration, biodiversity conservation and soil enrichment. Apart from these, it is a prerequisite for environmental sustainability as a "give and take" relationship is always established. Figure 8 shows a typical silviculture agricultural system (Quantitative tools: Growth models 2008).

3.6 The Biochar Fortification of Soil Approach

Biochar is a material produced through pyrolysis of biomass feedstocks (Luostarinen et al. 2010; Qayyum et al. 2014; Younis et al. 2014a, b; Danish et al. 2015; Abid et al. 2017; Danish and Zafar-ul-Hye 2020). Pyrolysis is the direct thermal decomposition of biomass in the absence of oxygen to obtain an array of solid (biochar), liquid (bio-oil) and gas (syngas) products. Biochar is a mixture of char and ash, but is mainly 70–95% C (Luostarinen et al. 2010). According to Lehmann et al. (2011), application of biochar to agricultural soils has not been practised in modern farming. However, the biochar technique (application of char) to farmland, according to the authors, is not a new concept. For example, certain dark earths in the Amazon basin

Fig. 8 Silviculture agricultural system. (Adapted (Quantitative tools: Growth models 2008))

Fig. 9 Biochar (WarmHeart Worldwide 2019)

known as "terra preta do indid" contain large amounts of biochar (Lehmann et al. 2006). These soils are exceptionally fertile compared to soils in these regions that do not contain biochar (Lehmann et al. 2003; Danish and Zafar-ul-Hye 2019). Figure 9 presents a typical biochar (WarmHeart Worldwide 2019).

Lehmann et al. (2003) topped C sequestration in the potential benefits of biochar, through the natural process of photosynthesis, including reduction of N_2O-CH_4 emissions from soils, net production of energy in form of bioenergy and increase in soil fertility, as well as yields of agricultural crops, increased microbial activity in the soil, improvement of water retention capacity in the soil, cation exchange capacity, durability of soil aggregates and reduction in erosion, fertilisation and nutrient leaching (Clapham and Zibilske 1992; Muse and Mitchell 1995; Hashmi et al. 2019; Zafar-ul-Hye et al. 2019, 2020; Meena et al. 2020a; Danish et al. 2020; Sultan et al. 2020).

Onwe (2016) evaluated effect of different rates of biochar and wood ash on soil properties, and yield of maize in Abakaliki, Southeastern Nigeria, observed soil C stock of 14.3 g kg^{-1} in control; 12.2 g kg^{-1} under 3 t ha^{-1} biochar; 16.4 g kg^{-1} in 3 t ha^{-1} wood ash; and 13.4 g kg^{-1} C in mixture of biochar and wood ash. Fowles (2007) explored black C sequestration as alternative to bioenergy, while Laird et al. (2010) examined impact of biochar amendments on the quality of a typical midwestern agricultural soil. Lehmann et al. (2006) described biochar soil management on highly weathered soils in the tropics, while Mankasingh et al. (2011) gave details of biochar application in a tropical agricultural region. On the other hand, Njoku et al. (2015) described the effect of biochar on selected soil properties and maize yield in an ultisol in Abakaliki, Southeastern Nigeria, while Rogovska et al. (2011) described the impact of biochar on manure C sequestration and greenhouse gas emissions. Sohi et al. (2010) reviewed biochar and its use and function in soil. Uzoma et al. (2011) described the effect of cow manure biochar on maize productivity under sandy soil condition. Yuan et al. (2011) assessed an acid soil with crop residues and biochar for soil improvement.

4 Carbon Forms: Going Back to Nature

In many cultural processes, civilisations are required for C sink. Even though there is impossibility of world without modern civilisation, championed by man’s quest for optimum use of natural resources, humanity stands in peril if we continue on “business as usual” in our anthropogenic activities, use of fossil fuel and biodiversity. As population spills over human comprehension, followed by global demand for food, clothing and shelter that contributes over 90% of gaseous emissions, C sink will be most contained if nature is to sit on its course devoid of constant human interferences.

Most of the world’s resources – air, land and water – are capable of regulating global C sink if most civilisations make optimum use of solar, wind and wave power as source of energy for land, air and sea travel. This can curtail global anthropogenic greenhouse gases to high proportions. The use of organic manure from plants and animals as alternative to synthetic chemical fertilisers will curtail global greenhouse gases emissions tremendously. Hence, agricultural revolution anchored on organic fertilisation only. The use of biopesticides as alternative to synthetic chemical pesticides for agriculture and industrial uses can curtail massive greenhouse gases emissions. The slash and burn agriculture and use of portable hand tools and implements in land preparation and post-planting operations, even though will look insane, but will reduce emissions from farm machines, tractors and post-harvest machines. The use of fabrics and building materials that are less dependent on forest resources and that can use rocks, sediments, soils, clays, debris of plants and animal wastes and can be knit-together by solar, wind and wave energy at local levels will reduce anthropogenic greenhouse gases emissions. The reduction in usage of clothings, houses and food beyond waste levels by greedy and insatiable mankind can address these problems. The rate of vacant clothes, houses and food that are sometimes destroyed to save international, national and local prices contribute to the problem. The luxury human lifestyle in wealth, travel, expedition and

Fig. 10 Nature. (Pexels 2019)

splendour where a King or Queen has estate as large as Nigeria contributes to the global problem. The fact that land is accessible and affordable to only less than 5% of world's citizens makes it difficult for individual to access land and land resources and the ability to feed oneself based on personal efforts as supermarkets are now built on factory lines and citizens live to work and not work to live. Figure 10 shows photo of nature at its wonders (Pexels 2019).

Going back to nature is not good news for capitalist who believe and trust on money and wealth that can last for millennia at the peril of world citizens. The world can be self-sufficient in food, shelter and clothing if world resources are accessible to world citizens at no price, tag or restrictions as mankind is mortal and lives for few years and gives space for new generations. The fear of survival of the fittest is worst with global nuclearisation of nuclear power, nuclear energy, militarisation and policing that contribute significantly to global greenhouse gases emissions. The worst scenario of politisation of global warming, climate change, rise in sea level and tsunami makes researches and alternatives to problems being the main problems themselves. But going back to nature requires everyone mathematical touch of mind and will mark the era of new human civilisation. It will sink C and make another "C gold" like the current "crude oil" or "fossil fuel" gold of the world in millennia to come.

4.1 Carbon Sink: Going Back to Nurture

For human civilisation that live on fear of returning back to "status quo" or ancient primitive civilisation anchored on "back to nature", the silver lining lies on falling back to "nurture". Yes, we can nurture our endowed natural resources – air, land and

Fig. 11 Nurturing nature with science. (Adapted (Allison 2012))

water – for modern civilisation that will spell the doom of "C terrorism". Yes, we can nurture our air, land and water resources through collective efforts and responsibilities at local, national and international levels based on our individual levels of civilisation. There should be no forced civilisation through local, national and international laws, legislations, edicts, loan, projects, activities and programmes that divert local citizens mind away from natural culture, spirit and soul of taming nature at domestic levels on individual and collective levels. The diffusion and enforcement of modern civilisations through gadgets and technologies, namely, ICT, mobile phones, televisions, radio, cinema, films and computers, have made modern-world citizens slaves to gadgets and technologies that siphon rather than add to their resources. World citizens live above their income on bank loans, credit cards, IMF loan, World Bank loan and Regional Banks loan to their perpetual generational doom that have taken them away from nurturing nature. This is the doom of mankind. Returning to tame nature takes patience and fortitude. To plant a tree, rear animals, grow crops on natural basis, use bicycles, trek or recycle natural resources takes ages to accomplish. But world citizens desire "wait and take" technologies and genetic engineering that are detrimental to nature's nurture. Nature is not a system that works on man's time, instincts and convictions. It takes time to develop and spread, hence, requiring patience and fortitude. This is not good for capitalists and money mongers who are not concerned on aftermath of their mess on the planet earth or who use their wealth and money to try to revise changes or mistakes predicated on their actions which at times are irreversible and irrevocable. Figure 11 is (Allison 2012) impression of nurturing nature with science.

The panacea to "C terrorism" in the world still lies between nature and nurturing nature. No matter the advances in science, technology and researches, there can be no solution to modern-day quest for global C holocausts not anchored on nature and nurture.

4.2 Between Nature and Nurture

In a fragile earth, there is impending decision between nature and nurture at all levels of civilisation at local, national and international levels. Civilisations must agree to accept and tolerate one another. Civilisations must be ready to take the consequences for their actions at all levels and regions. Civilisations must be ready to work hard to preserve and nurture their natural resources. Civilisations must be ready to develop at their space and comfort without any fear of competition and intimidation. Civilisations must be ready to depend on their own local food, clothing and shelter. Civilisations must be ready to depend on their culture, tradition, norms, dialects, languages, technologies and sciences without borrowed civilisations, culture, tradition, norms, dialects, languages, technologies and sciences. The era of "globalisation" is enemy to nature and nurture. Globalisation has impoverished instead of enriching world citizens. World citizens are now poorer than their ancient primitive ancestors who owed gold, diamond, silver, livestock, crops and plantations and lived freely and courageously based on hard work and natural endowments, unlike modern ones anchored on robots, machines, computers, industries, factories, supermarkets, high street and living to work culture and lifestyles.

Since man must remain to colonise the planet earth, the logic of literacy must be clearly separated from the logic of nature and nurture that lives in every man. Literacy, academics, knowledge, wisdom and intelligence mimic man, nature and nurture and serve as aberrations and shield to natural nature and nurture in human instincts. For civilisations to continue to live in fear and jeopardy of "C terrorism" is very dangerous. Time has come for us to live between nature and nurture and save the "C gold" for millennia citizens of the world through C sink. Figure 12 depicts Thedrmoshow (2018) description of "Nature v Nurture".

Fig. 12 Nature vs nurture. (Adapted Monique 2018)

5 The Future of Carbon Sink in Tropical Ecosystem

The future of C sink is very dicey, not only in tropical but other ecosystems of the world. This is because civilisations have come to believe and trust on the "Do as I say and not as I do". There are many cross-roads to "C terrorism". The one part leads to "global prosperity" and the second one to "global Armageddon". But the second one is very eminent in view of civilisations partitioning the world for natural resources, wealth, honour and fame. The fight between the giants (superpowers) and the rats (inferior powers) of the world is very terrifying and catastrophic. The robbing Peter to pay Paul scenario and mentality continues to cripple the world. To the actors, what is good for the goose is also good for gander. Figure 13 is (Cook

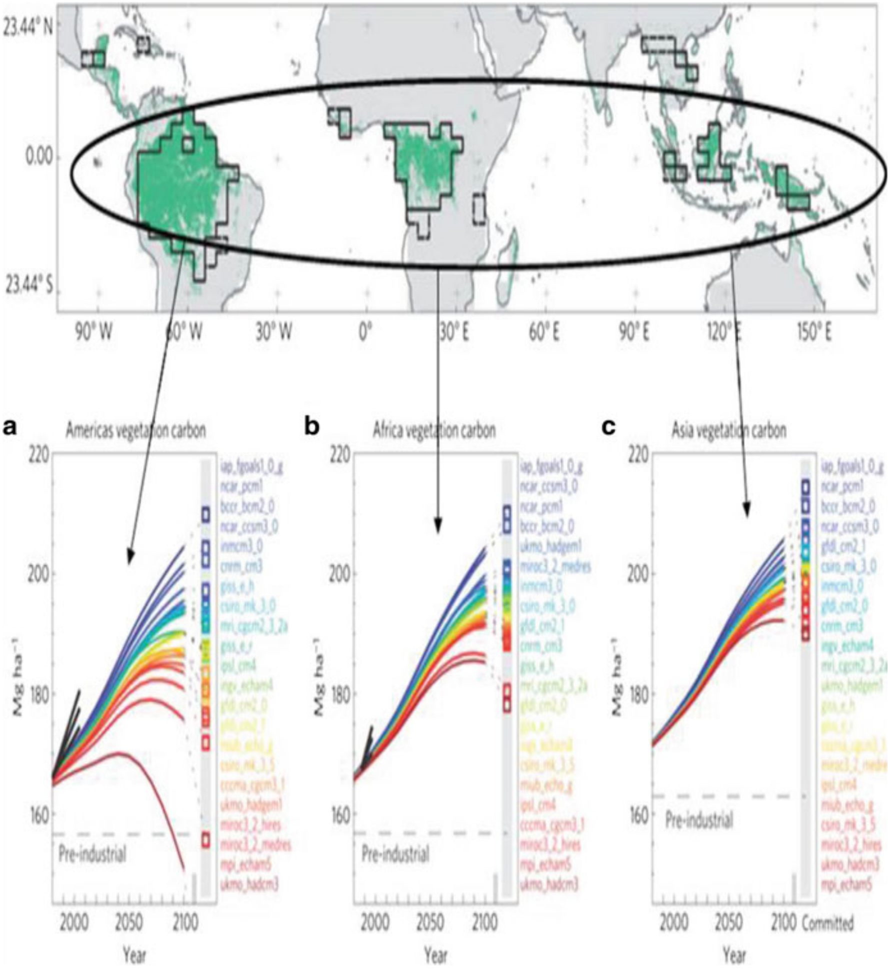

Fig. 13 Will tropical forests remain carbon sinks (Cook 2019)

2019) question “Will tropical forests remain C sinks”. Civilisations are now akin to competition for development and use of local, national and international resources. The searches, researches and writings to contain “C terrorism” is more of academic and political exercises that hunt and divide human civilisation.

The future of C sink lies on our hands and not on the pages of newspapers, newsletters, journals, books, televisions, radio, computer and phone. Can there be a collective world civilisation? The answer is “no”. Can there be a separate world civilisation? The answer is yes. Let us say “no” to force or imposed civilisations at all levels and use our resources judiciously for the next generations. Is there any need to think for next generations? The answer is yes. The previous generations thought for us by using natural resources judiciously that made the world better for us. We owe future generations the same magnanimity of ensuring they enjoy the natural resources we leave behind for them. Not only because it is necessary and desirable, but because we are living on a keg of gun powder of “C Armageddon” which we have greedily and deliberately created for ourselves. The cries and mourning to save the earth from “C terrorism and Armageddon” supersede that of the cries for “nuclear terrorism and Armageddon” as no nation or tribe or civilisation can wipe out its own tribe or generations, except by nuclear accident or holocaust. Again, nuclear arsenals are created and managed by man, but nature is no respecter of persons, tribes, nations, languages, beliefs, imaginations, sciences and technologies. None of these are capable of damming global scorching temperature or tsunami arising from collapse of sea levels.

6 C Sink as Panacea to C Stabilisation in Agroecosystem

From empirical science, C tinkering, C losses and gains, to C sink there is gain in C stabilisation in all agroecosystem. This is because plant biomass still remains the greatest veritable sink for greenhouse gases. The question of C stabilisation depends on the conditions we expose the soil which is the greatest sink and asset of man. The activities that lead to their losses must be less than activities that lead to their gains. That is the basis for initial question in the script “C losses and gains in dynamic ecosystem – Any hope for equoscience”. The “equoscience science” border on sciences and technologies will bring to equilibrium the net losses and gains to zero. This is very tempting and difficult. Figure 14 shows (Lal et al. 2018) view of C sequestration potential of terrestrial ecosystem.

Nevertheless, the controversies surrounding C sink and stabilisation give hope for humanity. It drives the engine that keeps the world awake 24 h a day for eternity. A child who gives the mother sleepless night must also be ready to experience sleepless night. Greenhouse gases is the child and world citizens is the mother. Greenhouse gases must continue to have “sleepless nights” as far as it keeps world citizens “sleepless nights”. Until both reach a consensus and agreement that will lead to their sink and stabilisation that will liberate world citizens from impending “C terrorism, holocaust and Armageddon”, till then, the future of C sink in agroecosystem remains a dilemma and nightmare.

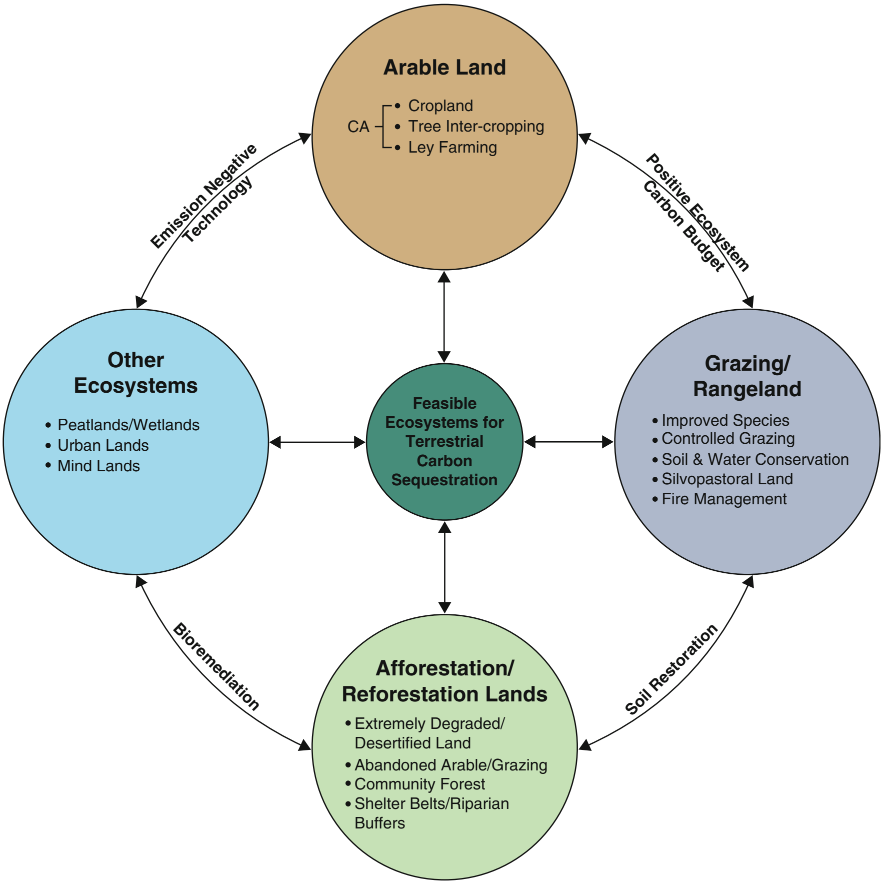

Fig. 14 The carbon sequestration potential of terrestrial ecosystem (Lal et al. 2018)

7 Conclusions and Future Prospects

C sink and stabilisation is vital for health and well-being of man. In fact, it is greater than food, shelter and clothing as nature is no respecter of persons, food, shelter and clothing and can sweep us into the Atlantic within seconds and twinkling of an eye. The world must rise up to the challenges of greenhouse gases, global warming, climate change, rising sea level, tsunami and impending C holocaust or Armageddon. To sink and stabilise C in soils just requires common and sensible respect for nature and nurture. All other gains will follow that will be beyond human comprehension. The leap for the future begins with you and me. The time is now.

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Methane Carbon Sink Distribution and Stability in Permafrost and Deep Marine Soils

Bhajan Lal

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Abstract

The presence of soil carbon(C) in permafrost and marine environment is not well understood, and thus their incorporation in the global C cycle is challenged. In this chapter, we briefly discussed the state of the art of soil C in the form of frozen C (CH_4 hydrates) in the permafrost and marine environments. The global

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distribution and estimate of CH_4 hydrates are discussed, alongside the dissociation potentials and its impact on climate change. The CH_4C sinks and dissociation in the sea and permafrost are also discussed. The sink shows that very few gas hydrate locations in the world are possible to release significant C to the atmosphere. Lastly, the possible applications of gas hydrate as a future energy source and C storage techniques are discussed. There are huge CH_4 frozen C in the marine and permafrost environment which are very vulnerable to dissociation owning to recent climate changes and may cause the release of a significant amount of CH_4 to the atmosphere.

Keywords

Climate change · Soil carbon · Gas hydrate · Methane · Permafrost · Marine sediments

Abbreviations

AOM	Anaerobic oxidation of methane
BGHS	Bottom of the gas hydrate stability
BSR	Bottom-simulating reflector
C	Carbon
CO_2	Carbon dioxide
GHSZ	Gas hydrate stability zone
Gt	Gigatons
H_2S	Hydrogen sulphide
H-I-V	Hydrate-ice-vapour
H-L_w-V	Hydrate-liquid-vapour
I-H-L_w-V	Ice-hydrate-liquid-vapour
IPCC	Intergovernmental Panel on Climate Change
Jg^{-1}	Joule/gram
LNG	Liquefied natural gas
M	Meter
Mpa	Mega pascal
OC	Organic carbon
ODP	Oregon Ocean Drilling Program
P	Pressure
PAGH	Permafrost-associated gas hydrates
P_c	Critical pressure
PCF	Permafrost carbon feedback
PETM	Paleocene-Eocene Thermal Maximum
PgC	Petagram of carbon
ppm	Parts per million
P_t	Triple point pressure
SCP	Soil carbon pool
sH	Structure H

sI	Structure I
sII	Structure II
SRZ	Sulphate reduction zone
STP	Standard temperature and pressure
T	Temperature
T_c	Critical temperature
Tg	Teragrams
T_t	Triple point temperature

1 Introduction

Soil C consists of the solid terrestrial organic matter deposited in soils around the globe. It generally consists of C from inorganic sources and organic matter. Soil C plays a critical role in climate change mitigation (which is the focus of this book). Other relevance of soil C is its use in constructing global climate models and biogeochemistry. Hence, soil C is a useful component in the global C cycle. There are recent alarms on the rise of C emissions in the world; it is believed that C emissions are at 2.3% per year (Ma et al. 2019; Meena and Lal 2018), while the C confiscation ability of soils in the world is in the range of 5–15%. Hence, a further rise in C emission may result in dangerous levels of warming which may be unfavourable for the society.

Generally, soil carbons are less focused on marine soils and permafrost soils. However, the Arctic and marine soils are reported to contain a huge amount of C, which when released could be dangerous to the existing C levels (van Huissteden and Dolman 2012). Therefore, in this chapter, we discuss briefly the state of the art of soil carbons in marine and permafrost soils. Huge quantities of OC (CH_4 and CO_2) exist in arctic soils, fluvial sediments (marine sediment), and peats in a frozen state. Interestingly, these soil carbon pool (SCP) is very susceptible to dissociation, i.e. they are highly unstable. Progressive actions in the marine and permafrost may lead to the release of an unknown amount of CO_2 or CH_4 to the atmosphere. For example, the thermal increase of the Paleocene-Eocene is believed to result from the permafrost C feedback (PCF) (Ma et al. 2019); however, very less information is known on the quantization of the present marine and permafrost C.

The permafrost is very uncertain and complex in its occurrence and processes. The permafrost covers about a quarter of the northern landmass; however, very little is known about its biogeochemical, hydrological, and geomorphological thwarting processes. Recently, the permafrost C feedback has been grafted into the climate prediction models. Estimates and predictions have shown that the permafrost soil C has doubled, and it is believed to be almost twice as the C present in the atmosphere. A threshold amount released in the atmosphere of about 1% is estimated to increase the atmospheric C content with 6.6–8.7 ppm. However, there are traces of C release in the atmosphere, with some experts showing evidence of a decrease in C pool in the permafrost of about 11–17% by 2100. However, the arctic is proven as a CO_2 sink of about 0.3–0.6 PgC/year (van Huissteden and Dolman 2012). The exact estimation of the permafrost C feedback is seriously needed to combat and comprehend recent climate changes. However, the permafrost C feedback represents about 148 ppm increase of C in the atmosphere. There are several articles which detail the present C pool and its lost processes in the permafrost; readers may refer to them for more information.

On the other hand, the world's rivers and marine sources deliver about 430 Tg/year of terrestrial organic carbon (OC) to the oceans. Just as marine OC is from primary production, only part of OC in the terrestrial environment endures remineralization and can be buried in marine sediments, especially in rivers and deep-sea fans (Berner 1982). Some reasons that account for the quantity of OC that could be stored are the physical structure and processes during deposition (rate of burial and organic matter composition). However, organic matter found in marine environments is more refractory due to its burial conditions (Burdige 2007). Mostly very few amounts of OC in marine environments are from terrestrial origin, probably due to the sheer magnitude present in the marine main production (Burdige 2007). The vast or majority of these unstable soil C in the permafrost and marine environment exist in the formation of CH_4 hydrates. Theses hydrates are known as a future energy source that may replace fossil fuel due to their abundance and threat to the climate when released to the atmosphere. Hence, in this chapter, we discuss the state of the art of hydrate and its possible contribution to climate change.

2 Terrestrial Permafrost

2.1 What Is the Permafrost?

The permafrost is defined as the ground or soil that has a constant temperature below 0 °C. The permafrost is known to cover about 20% of the Earth's terrestrial ground (Davis 2002). Due to the geothermal gradient of the Earth, it has a limit and very shallow depth. It is about 50 m deep vertically in its continuous form. However, in the discontinuous zone, both permafrost and non-permafrost are present at 350–650 m. The discontinuous region of the permafrost is mostly very easy to dissociate at unstable pressure and temperature environmental conditions. Mostly the location of the permafrost is very thin and close to its thawing point. On the other hand, permafrost may as well occur in the marine environment. When permafrost occurs in the marine environment, they are known as subsea permafrost.

The permafrost soil usually consists of a layer that is exposed to freezing in the winter and thawing in the spring or summer. This layer is called the active layer of the permafrost. The active layer seasonal changes affect plant rooting, hydrology, and OC decomposition and storage (Schuur et al. 2008). For instance, during winter, the active layer is found between two regions: the freezing air on top and the sub-zero permafrost at the bottom. By so doing the active layer goes through a heat transfer at its bottom and top which causes continuous freezing. These freezing or heating cycles may occur for several years and times according to the season. These changes in cycles are believed to aid or control the dissociation of frozen CH_4

C into the atmosphere; however, the dissociation mechanism or phenomenon is not well-known and understood (Mastepanov et al. 2008).

There are two types of C found in the present permafrost soil around the globe. The first type is the frozen-rich OC located in peatlands. The second comprises minerals soil carbons found within the permafrost. Due to the decreased decomposition of the highly concentrated anoxic environments, a huge OC-rich soil is formed in the peatlands. The physical formation of C-rich organic soil in the peatlands implies that the active layer of the permafrost consists of C layers that are buried at very deep depth and thus frozen permanently as permafrost.

The formation of permafrost would form peat structures consisting of ice at very deep depth, which would pause basal decomposition (French 2007). During the last glacial occurrence in boreal, there was an evidence of the onset of peatlands in the area (Connor et al. 2010). This is due to biological activity near the surface causing the deposition of C. On the other hand, the lower C soil mineral may also be present during the deposition via wind-borne dust and loess. When this happens the OC on the surface are further deepen and result in frozen permafrost. There is huge rich organic matter from plants, grassland, incorporating root, and animals buried below fluvial sediments in the regions of Siberia and Alaska. These organic matters have lasted for several thousands of years during the Pleistocene (Zimov et al. 2006; Meena et al. 2020b).

However, loess possesses high labile C due to its less subjection to decomposition. But loess generally has very low OC content. In contrary, peat-based permafrost has very poor labile C because they are prone to high decomposition before depositing as frozen permafrost. However, peat-based permafrost has very high C fraction. There are other traces of C deposition in the permafrost under deep peat organic soils evolved from lakebeds or cryoturbation accumulation (Walter et al. 2007). There is mostly high distribution of OC within the mineral layers deep down the permafrost. This high OC supports surface vegetation and is mainly caused or controlled by the cryoturbation of sediments present at the subsurface (Schuur et al. 2008).

2.2 Permafrost Methane Carbon Distribution and Inventories

In this section, the distribution and inventories or estimation of the amount of OC frozen in the permafrost is discussed in detail. The amount of OC trapped in frozen peatlands amounts to approximately 20–60%. However, the estimated amount of OC is less than 20% in frozen loess and mineral organic soil (Schuur et al. 2008; Meena et al. 2020a). It is worth noting that the estimation or quantification of the C in the permafrost is very difficult due to the heterogeneous behaviour of the permafrost and peat regions. Schuur et al. (2008) estimated the amount of C present in the permafrost areas as 1672 Gt C. They projected that the amount of C present in the frozen peatlands is about 277 Gt C. While about 407 Gt C was present in Siberian yedoma. The non-relict mineral/organic soils contained about 747 Gt C, and the amount of C in river deltas (consisting of deep alluvial soils) is 241 Gt C. All these estimations consist of the C soil on the surface of the permafrost.

Zimov et al. (2006) also predicted the amount of soil C in Siberian yedoma as 450 Gt C, which is in close agreement with the estimation of Schuur et al. (2008). They further reported that the C content present in non-peat and non-yedoma permafrost regions are approximately 400 Gt C. More improved and better predictions have provided a more reliable C content estimation in the permafrost regions concerning permafrost extent, soil type, and depth. For example, Tarnocai et al. (2009) presented that about 10.1×10^3 Km^2 area of 18.8×10^3 km^2 surveyed (about 70%) has a constant permafrost zone in Eurasia and North America. They estimated that the amount of C in the permafrost was about 1672 Gt C. The soil C in the top 3 m of the nonalluvial and non-yedoma permafrost is made of 1024 Gt C.

2.3 Changes in the Permafrost Thawing

Permafrost thawing is the main concern that exists for the future of the OC frozen in the permafrost. Especially the permafrost at the surface is the main area of focus. The dissociation of the permafrost is highly controlled by the recent alarm on climate change causing increasing temperatures around the globe. The dissociation of this permafrost could cause the release of huge amounts of CH_4C into the atmosphere (Goulden et al. 1998). It is believed that the dissociation of the present CH_4C has been initiated and is ongoing with a gradual increase in the depth of the active layer (Jorgenson et al. 2006). However, the amount of C in the peatlands could be very much affected due to the increasing temperatures of the climate and soil drainage change response. The critical disadvantage associated with the permafrost thawing is not just the increasing dissociation of the active C layer. But the thawing could interrupt in the physical and hydrological structure of the soils. These may cause the lakes and wetlands to increase to wider extends and thus lead to high CH_4C emission potentials (Zhuang et al. 2009).

Interestingly, these high latitudes are sources of CH_4 but sink for C dioxide. However, if climate change persists in the near future, more CH_4 release might increase. These might be controlled by a wetter and warmer climate for a long period. Since the effect of climate change on the permafrost C and CH_4 dissociation are very complex to understand, better studies and evaluations on the mechanisms on the effect of climate change on CH_4 dissociation is required. Such studies are recommended to include the changes in phases of the permafrost, the physical impact of the soil moisture on the permafrost, and the surface vegetation on the permafrost. The sluggish process of soil aggregation, either through organic peat absorption or by wind-blown deposition, ensures that today's permafrost C production has taken place for several thousand years.

Until current, several ice wedges in North American permafrost have dated back to 700,000 years. It means that many glacial-interglacial stages have undergone at least some permafrost and extended colder times than today. Nonetheless, Jorgenson et al. (2006) describe large areas of Alaska permafrost depletion that have existed since 1700, suggesting vulnerability to fairly mild climatic cycles. Processes regulating permafrost C susceptibility may be divided into incremental adjustments such as talik forming, active layer deepening, and abrupt changes such as a fire. Such incremental and abrupt shifts in effect would be addressed. Productive layer deepening is a clear incremental thawing at successively deeper stages owing to higher temperatures (improved thawing in summer and decreased re-freezing in winter) and prolonged over-freezing seasons.

The soil moisture will rise through simple thawing, while the moisture-holding potential increases with the organic soil component as the vegetation raises. The change in the moisture of the soil contributes to potentially increasing heat of the soil; this in effect results in a quicker freezing condition. This as well increases the soil's thermal conductivity, through thermal relation to the environment, resulting in the counters of the existing elevated heat of the soil. As a result, a higher thawing effect occurs in summer, which could not be offset by the refreezing of the winter. Increasing snowfall in autumn (as expected by certain climate models) contributes to decreased insulation and thus less refrigeration. This process, rather than the air temperature, was established as the most probable source of recently reported that the soil temperature in North Atlantic has risen. On the other hand, Schuur et al. (2008) claim that mechanisms that defrost C from a perpetual frozen environment are faster than the immediate temperature susceptibility of C release. Suggesting the process as very important, which needs critical attention.

The simplest known method of C emission by defrosting is active layer deepening. This input happens as the decomposed organic matter in the soil produces heat energy which adds more heat to the soil. In the case where this occurs at a well-protected soil depth from the environment, the heating attains more energy to achieve a self-sustaining strength that results in more thawing (Khvorostyanov et al. 2008). In areas such as upland, the presence of albedo at the shallow surface of the soil can cause thawing over a prolonged duration (Sturm et al. 2001). Interestingly, soil thawing and wildfires could be further enhanced by increasing vegetation. Nonetheless, a further rise in the OC composition of the soil could occur in wetlands where the moisture of the mosses is maintained. The mixture behaviour of the soil vegetation also controls the degradation properties of the CH_4 yields. It determines whether anaerobically (yielding CH_4) or aerobically (yielding C dioxide) will occur in the degradation process. However, a sudden shift in the environment occurs as a result of the presence of fires and thermokarst. The actual deterioration of the soil surface due to permafrost decomposition is known as thermokarst.

This happens due to changes in the heat balance of the active soil layer, contributing to the creation of lowland reservoirs and probably even to the loss of overlying trees. This relies on the distribution of ice and thaw, which in effect relies on surface materials, geology, and topography (Connor et al. 2010). Ice saturation is a major factor that controls the occurrence of thermokarst in the permafrost. This is because the existence of high ice saturation causes an easy response of the active layer to elevated atmospheric heat coupling and lower permafrost affects the soil heat power. It profits permafrost soils and sediments that are discontinuous but poses to be disadvantageous to rugged regions, mountainous regions, and persistent permafrost zones. Thawing will cause increasing lake water levels. The melting of thermokarst also causes flooding with water or reduced lakes if the frozen soil covers the bottom of the lake, causing it to drain (Connor et al. 2010).

All of these occur during thawing depending on the position, depth, and permafrost ice quality. Wildfires can possess rapid and noticeable permafrost melting effect on the environment. Additionally, to the effect on biomass, the presence of fire may destroy the landscape layer of dead litter that created protection to the soil before to the fire. Fires that occur in North America have also been found to rise in the last decades of the twentieth century in both the region of combustion and the intense volume of burning. This rise was due to anthropogenic global warming and is also expected to arise in Siberia and which Soja et al. (2007) recorded a significant spike in severe seasons of fire and a lengthy-term growing trend in documented region burns.

Changes in potential fire regimes in boreal environments would be dictated by correlations amongst temperature, soil moisture, forest cover, and structure. Longer predicted fire seasons and greater seasonal intensity all contribute to a possible rise in C pollution from fires. Talikes usually apply to horizontal indefinitely unfrozen areas between both all year around the frozen active layer above and at the bottom of the frozen permafrost. They are growing in transitional permafrost regions but unusual in persistent permafrost regions (French 2007). When the active layer heightens and can no longer completely refreeze throughout the winter, talik development can arise when increasingly deeper layers of soil stay indefinitely unfrozen throughout the year. Taliks will affect subsurface infiltration and provide year-round soil respiration moisture, which ensures that degradation development of CH_4 and C dioxide will begin in the winter.

The most significant predictor of how the release of frozen CH_4C occurs is how the degradation continues aerobically or anaerobically, which usually relies on whether or not thawing permafrost becomes filled with water. It in effect depends on the subsurface structure of the soil and as to melting has enabled higher drainage. Generally, in the anaerobic environments, a huge portion of the soil OC decay is released as CH_4; however, this released CH_4 does not get to the atmosphere. The migration of oxygen into the soil and the movement of CH_4 out is propelled by the plant tissue and soil composition. When CH_4 percolates into adequate soil depth with appropriate oxygen content, it may be oxidized to C dioxide before entering the atmosphere. When CH_4 is formed at extremely high proportions, it may create bubbles and that may be discharged into the environment by boiling.

2.4 Permafrost Estimations

Current permafrost simulation methods utilize various frameworks that concentrate on specific issues from low to high scales and shorter to longer periods based on biogeochemical or physical mechanisms. Lawrence and Slater (2005) carried out a possible prediction of the survival of the permafrost in the Arctic. They expect a 90% decrease in the permafrost scale by 2100. Although the model did not simulate C cycles, there were no related predictions of C dioxide or CH_4 release, but Lawrence and Slater (2005) found additional feedback from local heating intensified by the melting of sea ice and ensuing the reduction albedo. Burn and Nelson (2006) and Delisle (2007) claimed that the estimations provided by Lawrence and Slater (2005) were overestimated due to the minimal modelling of the thermal fluxes of the deep soil. Lawrence and Slater (2005) react by noting that permafrost depths below 3.5 m were not considered in their modelling estimations.

This simulation also illustrates the potential for substantial relatively close-surface permafrost thaw, thus highlighting shortcomings in permafrost coverage in the general context of the Earth's surface structure. Refer to model simulations and the existing risk analyses; Schuur et al. (2008) claimed that about 50–100 Gt C would be released into the atmosphere through the melting of the permafrost by 2100. Concerning self-sustaining biological warming by the decay of organic matter which indicates that a higher percentage is more probable to occur (Khvorostyanov et al. 2007; Meena et al. 2018). Tarnocai and Stolbovoy (2006) have a common volumetric estimation of 48 Gt C permafrost peatland CH_4 C emission in Canada for the twenty-first century, compatible with the low lability of the peat CH_4 C reserve. Zimov et al. (2006) predict that when thawing, yedoma will emit all its amount of C within several years. According to Dutta et al. (2006), 40 Gt C will be released with the next four decades by the thawing of 10% permafrost deposition of Siberian yedoma. It relies on the high CH_4 C lability in yedoma and the decomposition contributing to bacterial respiratory warmth, which accelerates the thawing cycle.

Lawrence and Slater (2005) estimated a higher order of magnitude melt intensity. However, their predictions were criticized as underestimations by several authors. One such author is the work by Khvorostyanov et al. (2008); they proposed a model to simply predict the thawing in the permafrost specifically for the permafrost in the yedoma area. By using an ideal constant warming model ranging from 3 to 8 °C/per century, they claimed that 75% of the original 500 Gt C of frozen Chad has been emitted over the next 3–4 decades. The total emission rate was calculated to be around 2.8 Gt C per year; this is around one-third of the actual levels of C dioxide production from fossil fuel combustion (Khvorostyanov et al. 2008). About 92% of the volume of C emitted in the form of CO_2 between 2100 and 2200 is in the form of CH_4. In this situation, the anaerobic deposition of CH_4 is affected not by contamination of water but by a shortage of oxygen in the waters where the decay happens.

No average regional estimation was mentioned as this was a location-level analysis, but if this were to occur over a yedoma region of 1 million km^2 (Zimov et al. 2006), it would lead to 236 Gt C emitted throughout 100 years. Ise et al. (2008) used a model that is based on hydrological and thermal data. The model did not consider the under heating and surface drying conditions. The study suggested that the feedback from organic CH_4C dissociation and soil hydrological and thermal properties may worsen the loss of peat, especially during a very dry climatic atmosphere. In their models, the initial burst of CH_4 is emitted in reaction to warming, but much of the C is subsequently released as C dioxide as the soil layer dries and the decay will continue aerobically.

An attempt by Wania et al. (2009) resolves both the biogeochemical and physical dimensions of the experiment by expanding the Lund, Potsdam, and Jena vegetation models to incorporate eight more O-CH_4 soil layers within the upper (2 m) and increasing to a depth of 10 m with a clear evaluation of peat and non-peat hydrology and the effect of C content on soil products. Such improvements made it possible for the model to accurately predict the surface temperature and permafrost level and even to boost the C equilibrium in frozen environments. This model predicted major losses (> 60%) of permafrost in the 45 °N–60 °N area, also under the B1 emission scenario. Huge losses also existed in the area of 60 °N–75 °N; however in the north of 75 °N, amid substantial soil warming, sediment temperatures stayed enough below freezing that no permafrost loses occurred.

3 Fundamentals of Methane Carbon Cycle

C is a component in CH_4 structure, bonded with four hydrogen atoms. Generally, CH_4 is regarded as a major greenhouse gas, which is also the major component in natural gas streams. CH_4 has a limited life span compared to C dioxide; also, it has less concentration in the atmosphere but well-known to be about 30 times stronger than C dioxide. However, upon entering the atmosphere and mixing with oxygen, CH_4 can convert to C dioxide by reaction with oxygen as described by the equation below:

$$CH_4 + O_2 \rightarrow CO_2 + H_4 \tag{1}$$

The main sources of CH_4 gas are the permafrost, marine environments, plants, and animal farms. In all these sources the CH_4 is formed via the decomposition of organic animal and plant matter. Places such as mudflats, marches, sewage treatment plants, and leakage from natural gas pipelines and oil wells also produce CH_4 into the atmosphere. In the artic areas and marine environments, CH_4 is usually present as methyl clathrate. These methyl clathrates CH_4 gas compounds are frozen into like ice compounds under favourable pressure and temperature conditions. They can exist very deep within the Earth. These types of CH_4 C form the core of this section, with much emphasis on their effect on climate change. Thus, these methyl clathrates are known as frozen Cherein.

The existence of CH_4 displays a significant role in the C cycle of the Earth. Generally, the C cycles describe the perpetual changes of C amongst the inorganic and organic pools in the geosphere, atmosphere, hydrosphere, and terrestrial biosphere. The transformation of C from CO_2 in the atmosphere is quite fixed in the biosphere. The organic matter present in the biosphere may undergo decay, causing the C to be converted to CH_4. However, this process may depend on the environmental conditions of the biosphere system. The organic matter having undergone the decay process will convert the stored C in the organic matter to CH_4, which also by reaction with atmospheric or oceanic oxygen will change to C dioxide. The amount of CH_4 released into the atmosphere is governed by the CH_4 formation rate,

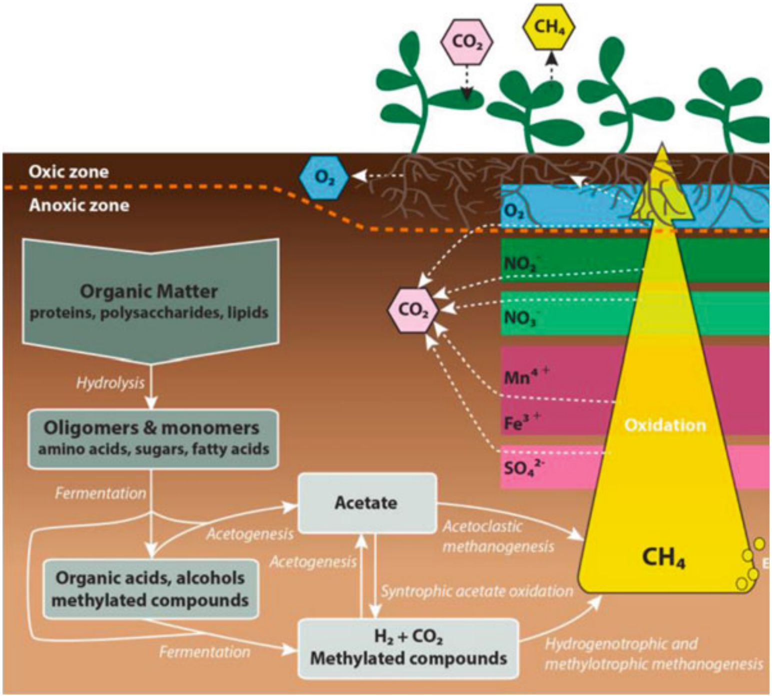


Fig. 1 Methane production, conversion/reaction, and migration process to the atmosphere. (Adopted Dean et al. 2018)

migration rate to the atmosphere from source of formation, and the rate of conversion during migration (Fig. 1). These factors are a key issue that affects the glacial cycle, by monitoring the CH_4 releasing capacity.

The unstable release of CH_4 to the atmosphere may be a threat to climate change owning to global warming. However, the CH_4 gas removal rate in the atmosphere is one main critical effort to drop CH_4 concentrations via hydroxyl radical, somehow causing a balance in the atmosphere. However, in this chapter, we focused more on CH_4 release for marine and permafrost environment (frozen carbon) and its possible impact on the climate and the C soil cycle.

4 What Is Frozen Carbon or Gas Hydrates?

Frozen C is known as any form of C (CH_4) that exist in a frozen state, which is mostly present naturally in the permafrost and marine environments. Gas hydrates are very important regarding the huge CH_4 C reservoirs that relate to ocean-atmosphere environments with much attention on global climate concerns. Gas hydrate is a solid crystalline compound or substance which is formed by the physical combination of guest molecules (low molecular gases such as CO_2, CH_4, H_2S, etc.)

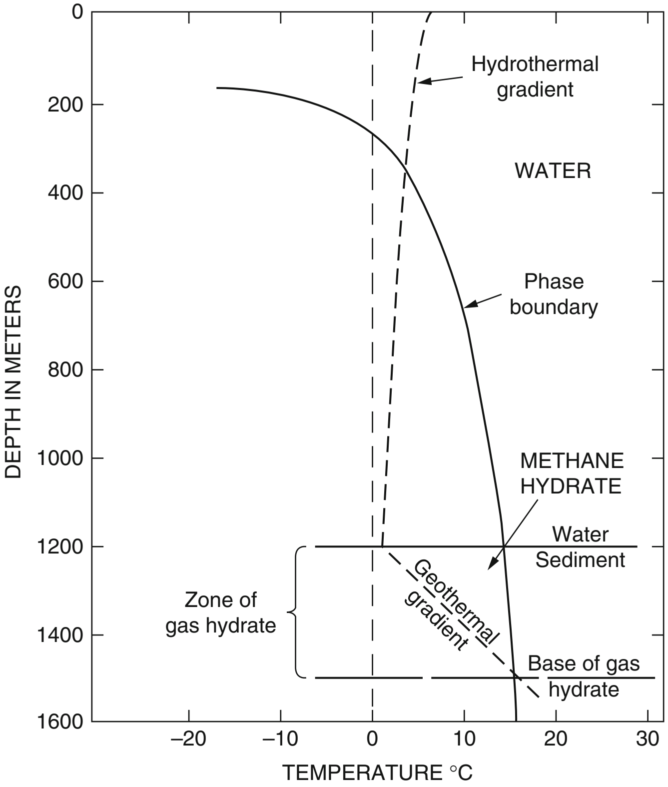


Fig. 2 Natural hydrate stability conditions

and host hydrogen-bonded water molecules at low temperature and high-pressure conditions (Bavoh et al. 2016b, 2019b, 2020). C in CH_4 is the main natural gas hydrate former compared with other hydrate formers. The presence and existence of CH_4 hydrates have been proven and characterized in abundance in the permafrost and shallow marine depths. Gas hydrate stores a large amount of CH_4 within its lattices. 1 m^3 of CH_4 hydrates stores about 180 m^3 of CH_4 gas at standard temperature and pressure (STP). This describes the huge amount of gas stored in hydrate forms.

Few depths below the seafloor in the deep-water sediments are the host and favourable environments for CH_4 hydrate formation and stability. This region normally has temperature and pressure conditions with thermodynamically favours CH_4 hydrate stability, especially at depths in the range of 300–600 m below the continental slopes and within and beneath permafrost at high northern latitudes. The CH_4 hydrate stability zone phase behaviour is shown in Fig. 2. A critical observation of the temperature and pressure profile in Fig. 2 shows that CH_4 hydrate can be very prone to perturbations, hence making them very unstable. An increase in the ocean/air temperatures and fluctuation in sea levels (pressure) can alter the stability of CH_4

hydrates and possibly lead to C release. This suggests that a small shift of the hydrate phase behaviour in the permafrost and marine hydrate sediments may be dangerous to the environment (Ruppel and Kessler 2017).

The C sequestration potentials of gas hydrates are very huge over half of the globe's mobile carbons from the soil, fuels, land biota, and peats. However, these estimations and claims are based on aged methods or techniques. With respect to the fragility of CH_4 hydrates arising from its dependence on seafloor temperature and pressure conditions, large amounts of stored C in the form of CH_4 could be released via gas hydrate dissociation at shallow depths of hydrates in the permafrost and marine environments. This dissociation of gas hydrate is a major threat to global warming. Also, a very huge amount of gas hydrate dissociation is mostly described due to warming, which could also cause the potential release of a significant amount of CH_4 in the atmosphere. Therefore, recent actions have been adopted to deal with the dual impact of gas hydrate dissociation on affecting and promoting global warming. This action is known as a catastrophic approach to the interaction of the climate system with global gas (Ruppel and Kessler 2017).

4.1 Gas Hydrate Formation Process and Structures

4.1.1 Gas Hydrate Structures

CH_4 hydrates are formed when CH_4 gas molecules (known as guest molecules) interact with water at pressures greater than 0.6 MPa and temperatures below 27 °C. Generally, the water molecules around the CH_4 molecules trap the CH_4 by forming hydrogen-bonded network cages (Bavoh et al. 2019a, c, d). However, there is no chemical reaction between the CH_4 and water molecules. However, depending on the gas mixtures coexisting with CH_4, different hydrate cages could be formed (Bavoh et al. 2016a, 2018a, b; Khan et al. 2017). The three basic gas hydrate structures that could be formed are shown in Fig. 3. They are structure I, structure II, and cubic structure H.

However, since most natural gas consists mainly of CH_4, the cubic structure I are mostly formed in the Earth's natural environments. Mostly structure I consist of gas molecules with sizes ranging from 0.4 to 0.55 nm. However, the presence of other gases such as propane and iso-butane may result in cubic structure II, while in the presence of cycloheptane, structure H might be formed. Therefore, sI would be further discussed and focused in this chapter.

The fundamental building lattices of hydrate (structure I and structure II) are pentagonal dodecahedra (5^{12}) hydrogen-bonded water molecules. Thus, it is made up of 12 pentagonal faces which are very prone to vibration and rotation, but less translational motion. In structure I the fundamental pentagonal dodecahedra structures are connected by their vertices, while in structure II they join by their faces. However, all the cavities are filled by the guest molecules to avoid hydrogen bond breakage and strain. Hydrogen bond breakage and cracks arising from inconsistent cavity filling cause the formation of hexagonal faces which helps to prevent cavity strain. In structure I of CH_4 hydrates the hexagonal faces have two faces

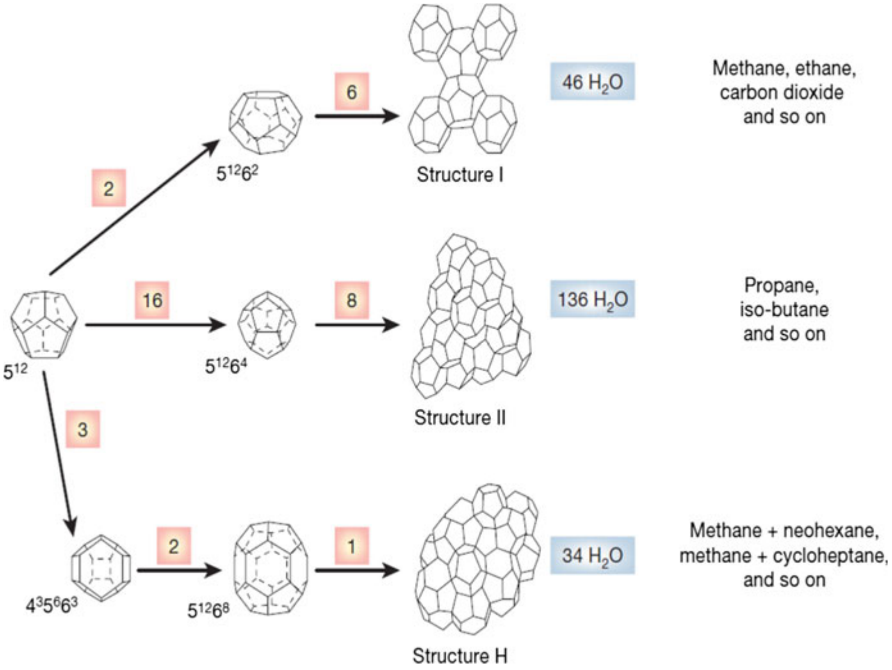


Fig. 3 Basic gas hydrate structures

($5^{12}6^2$), while in structure II it has four faces ($5^{12}6^4$). Due to the presence of larger gas molecules, the cages may contain the pentagonal dodecahedra and hexagonal faces at different ratios. In sI, their ratio is $2•5^{12} + 6•5^{12}6^2$, while is structure II, it is $16•5^{12} + 8•5^{12}6^4$. Every cage is mostly filled with one guest molecule, but the possibility of multiple guests in one cage is sometimes observed. In all hydrate structures, the presence of water is 85% and that of guest or CH_4 is 15% at a maximum cage occupancy. These engagements of the guest molecules mostly take place at the water-gas/CH_4 interface. The phase behaviour of thermodynamic conditions of hydrate formation and stability are properties dependant on their cage occupancies.

4.1.2 Simple Methane Hydrate

The type of guest molecules present determines the type of gas hydrate structure that can be formed (Khan et al. 2018; Bavoh et al. 2020). Since this work deals with sI hydrates formed from CH_4, only such gases would be considered. CH_4 hydrates were first measured by Villard (1888) in 1888 alongside ethane, ethylene, and acetylene.

CH_4 forms sI hydrate as a simple hydrate under appropriate pressure and temperature conditions and occupies both small and large cages of sI. It must be stated that the simple hydrate of CH_4 always occupies the small cavity of sI (5^{12} diameter ratio is 0.86) more than larger cavities due to its small diameter size. For complete hydrate

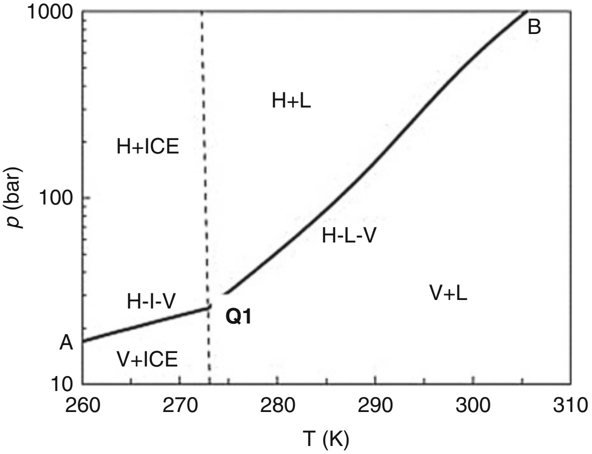


Fig. 4 Hydrate phase boundary condition of methane

cavities occupancy, CH_4 hydrate has a chemical formula as $CH_4.5.75H_2O$ and $CH_4.7.67H_2O$ for only large cages filled. The hydrate phase changes of CH_4 and water in the hydrate stability region is bounded by the H-I-V, H-L_W-V. CH_4 hydrate has one four-phase equilibrium points: quadruplet point, Q_1 (I-L_W-H-V, located at 272.95 K and 2.56 MPa). However, the triple point and critical point of CH_4 is at $T_r = 90.96$ K and $P_r = 0.0117$ MPa and $T_c = 190.56$ K and 4.599 MPa, respectively, as shown in Fig. 4.

4.1.3 Methane Hydrate Formation Process

The fundamental conditions needed for CH_4 gas hydrate formation include the presence of high pressure, low temperature, an adequate amount of water, and guest (CH_4) gas molecules (Bavoh et al. 2017, 2018b; Broni-Bediako et al. 2017). Interestingly, CH_4 hydrate formation process does not involve chemical bonding, rather a physical combination between the water (host) molecules and guest (CH_4) molecules, held together via van der Waals forces of interaction. There is always an allowable space that enables the guest molecules to spin freely in the cages of the hydrogen-bonded hydrate water molecules. Since CH_4 hydrate formation is considered a pure crystallization process, two main stages of formation are considered: (1) CH_4 hydrate nucleation process and (2) CH_4 hydrate growth process. The next section further discusses these processes in detail.

Just like any other crystallization process, the nucleation of CH_4 hydrate is mainly described as a microscopic phenomenon. It involves an initial formation of a smaller number of molecules at a microscopic level. The formation of smaller molecules keeps multiplying and sticking to each other until a critical hydrate nucleus is achieved for further CH_4 hydrate growth to commence. The time it takes for a visible critical hydrate nucleus to form in the system is known as the nucleation or induction time. At the induction time, the CH_4-water interactions have been fully fused by the small hydrate clusters to assume a critical size (Sloan et al. 2008).

Interestingly, the CH_4 hydrate nucleation process is a probabilistic/stochastic phenomenon that is highly time dependant and can occur after several seconds,

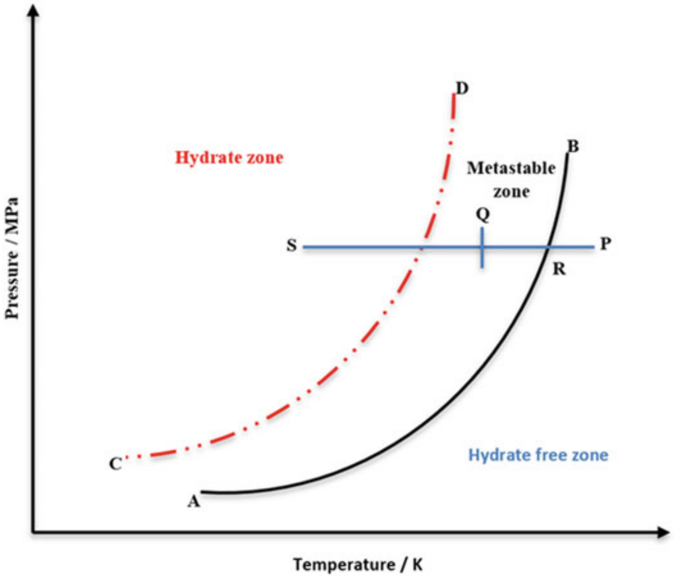
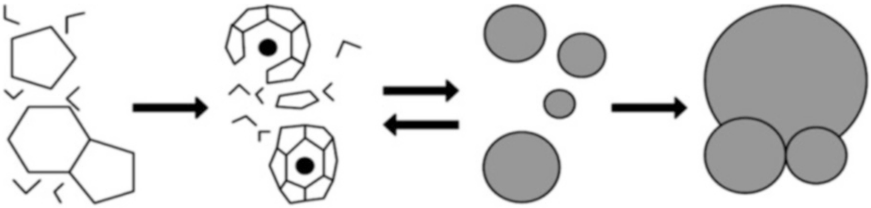


Fig. 5 The effect of subcooling on methane hydrate nucleation/formation, AB, equilibrium line; CD, spinodal line

minutes, hours, or days. The time taken for gas hydrate nucleation to occur mainly depends on the system, guest molecule, liquid phase composition, and agitation conditions. Generally, the probabilistic behaviour of CH_4 hydrate formation is controlled by the level of metastability present in the system. The metastability is described as the time taken for a non-equilibrium state to persevere. The metastable state is what mainly controls the hydrate formation process.

The pressure versus temperature profile in Fig. 5 can be used to understand the CH_4 hydrate nucleation and metastability behaviour under hydrate formation conditions. The hydrate equilibrium profile denotes the line AB in Fig. 5. The thermodynamic spinodal profile denotes the line CD. This line is used to represent the end of the system metastability zone. At the beginning of the hydrate formation process (point P), the system is believed to be superheated; thus the temperature of the system is very high and does not support CH_4 hydrate nucleation. To the left of the line, CD is the hydrate formation region. Fast hydrate nucleation which is followed by a rapid growth process when the system is set to the left because of the high driving force. A point Q is the metastability zone, which exists between the thermodynamic spinodal curve (CD) and the hydrate formation equilibrium curve (AB). At this point, the system is stuck in a probabilistic stage on whether to form or not to form CH_4 hydrate nuclei. When the system is able to overcome the metastable zone instability, the nucleation process is fast completed, and the hydrate nuclei cells agglomerate to achieve a metastable nucleus.

Another key to understanding the reason why some guests (gases) form better stable hydrate than others is the guest molecule solubility in water systems (Sloan



A. Initial condition: Pressure and temperature in hydrate forming region, but no gas molecules dissolved in water

B. Labile clusters: Upon dissolution of gas in water, labile clusters form immediately.

C. Agglomeration: Labile clusters agglomerate by sharing faces, thus increasing disorder.

D. Primary nucleation and growth: When the size of cluster agglomerate reaches a critical value, growth

Fig. 6 The labile cluster nucleation hypothesis of gas hydrate nucleation and growth process. (Christiansen and Sloan 1994)

et al. 2008). It is established that gas hydrate nucleation process generally occurs at the vapour-liquid interface (Sloan and Koh 2008). According to Christiansen and Sloan (1994), a better and simple way to describe the hydrate nucleation process is by studying the Labile cluster nucleation hypothesis. This hypothesis was developed by Christiansen and Sloan (1994) and has been used as bases to explain the hydrate nucleation process. The bases of the model are built on the idea that water (host) molecules surround the guest molecules that are dissolved in the water. This for some time allows the system to grow and reach a critical crystal radius, as illustrated in Fig. 6. The onset of a stable hydrate critical size represents the end of the hydrate nucleation process. After which hydrate growth process is said to initiate.

Apart from the conditions needed for hydrate formation, factors like enough mixing or vibration can enhance the hydrate formation process by providing fresh interfacial gas + liquid + crystal structures for a good surface activity for gas hydrate formation. Other particles such as sand may also serve as a nucleation site and will result in promoting hydrate formation. In addition, the presence of free water could cause more hydrates to form; however, these factors are just gas hydrate formation enhancers and not necessary the condition needed for hydrates to form.

After hydrate critical nucleus are formed in the system, the nucleus is then caused to grow into large hydrate crystals, since the positive Gibbs free energy has been overcome. These hydrate nuclei begin to take in for guest molecules causing a stable hydrate solid crystal. The growth of gas hydrates is controlled by the pressure, interfacial area, temperature, water history, vibration/agitation, and the subcooling degree. As the gas is taking to form more hydrate crystals, the pressure in the system begins to reduce sharply as shown in Fig. 7. When a constant pressure is achieved, it is believed that the hydrate growth process is complete and retarded (Sloan and Koh 2008). The hydrate growth process is purely controlled by mass transport of the guest to the hydrate surface interface. However, a heat transfer process is also involved with an exothermic heat release from the system due to hydrate formation.

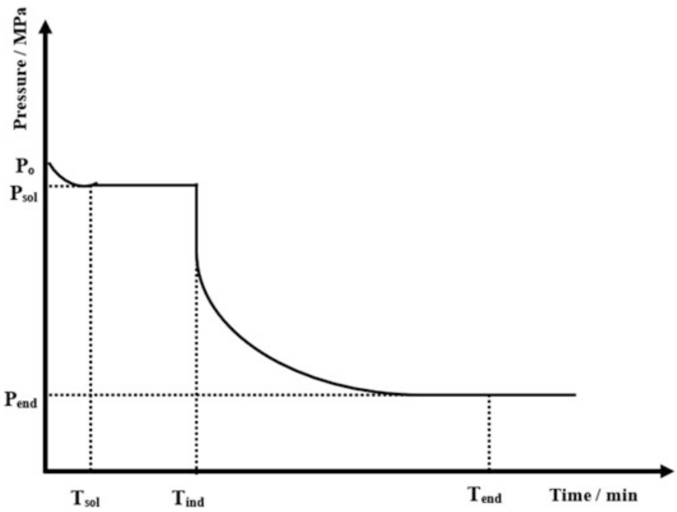


Fig. 7 Pressure versus time profile during methane hydrate formation nucleation and growth process

5 Distribution of Natural Gas Hydrates

The occurrence and estimation of gas hydrate is a major challenge for evaluating their effect on the climate. This fundamental information is needed for the quantification of CH_4 hydrates in the global C cycle. According to Yang et al. (2010), the majority (99%) of CH_4 hydrates are formed in marine sediments. They mostly exist at depths above 300–500 m depending on the latitudes on the respective continental slope. At higher latitudes the pressure is high, and thus they can be formed at lower depths compared with low to moderate latitudes. Generally, the area or region of temperature and pressure conditions favourable for hydrate formation and stability is known as the gas hydrate stability zone (GHSZ) on continental. On the other side, the permafrost region has very low temperature conditions which favour gas hydrate formation even at atmospheric pressure. However, at downslope, the gas hydrate stability zone could be increased as pressure increases and may stretch out to several water levels deeper than 1000 m, thus causing an easy condition for hydrate to form in presence of OC on the continental margins. By means of the rain of phytoplankton, the OC is supplied to the sediment. Also, the OC is usually transported from the continent's terrestrial sediment. C dioxide is also formed via the remineralization of the OC in sedimentary rocks, which also leads to the formation of CH_4 in sediments by microbial processes, resulting in the reduction of C dioxide content. Microbial CH_4 generally forms at elevated temperatures using similar mechanisms such as natural gas. This is generally the kind of processes found in the recovered gas hydrate. Generally, the gas hydrate stability zone in marine sediments are critically evaluated and estimated with care, particularly in vertical distribution. When characterizing vertical distribution profiles, the gas hydrate stability zone is highly differentiated from the actual gas hydrate occurrence zone due to the presence of enough water. To ensure hydrate formation in dissolved CH_4, the presence of conditions of excess CH_4, sufficient water, and favourable temperature and pressure must be fulfilled. In addition, the excess CH_4 must be soluble in the surrounding pore waters (Zatsepina and Buffett 1998; Xu and Ruppel 1999; Klauda and Sandler 2005). Thus, the physical chemistry and thermodynamics of the sedimentary section defines the area of the gas hydrate stability zone.

In some cases, gas hydrate can form at the bottom of the hydrate stability zone when there is a significant amount of dissolved water present. But this process normally takes very long period for hydrate nucleation and formation (Nimblett and Ruppel 2003). In marine sediment environments, CH_4 flux controls the upper part of the gas hydrate region and a biogeochemical process called the presence of a sulphate reduction zone where CH_4 is digested by microorganisms. However, areas such as highly saturated hydrate regions and fractured rocks are exceptional. One challenge in gas hydrate formation is the ability of CH_4 to saturate pore spaces present in the sediments. In both homogeneous and heterogeneous sediments, the saturation of CH_4 is very less; hence the permeability mostly disturbs the gas hydrates distribution. Also, the presence of clays, fine-grained rocks, and saline concentrated pore water prevents gas hydrate formation. On the other hand, the presence of sand (coursed-grand rock) and high permeability has a fast advection and thus possesses high gas hydrate saturations (Xu and Ruppel 1999).

Generally, the total quantity of CH_4 hydrates formed in the gas hydrate stability zone is less than the amount of available pore space. About 1% of the permafrost is believed to constitute the total amount of hydrates that exist in the Northern regions (Ruppel 2015). The lowest PAGH has been predicted to fall deep within the permafrost zone in about a few hundred meters. Permafrost that covers several hundreds of meters allows a stable gas hydrate formation beneath it, with a consideration of the geothermal gradient prevailing there. A presumable movement of CH_4 to shallower depths from underlying conventional gas reservoirs which is host to thermogenic gas allows most of the PAGH to be formed by the "freezing in place" of CH_4 (Boswell and Collett 2011; Ruppel 2015).

5.1 Amount of Methane Carbon in Natural Gas Hydrates

In addition to the occurrence and distribution of gas hydrates, quantification of CH_4 in gas hydrates around the globe is important in evaluating the effect of climate interaction with hydrates in marine and permafrost areas. Boswell and Collett (2011) predictions have estimated a few orders of magnitude. Earlier CH_4 hydrate estimation was very high compared with recent predictions. The earlier methods assumed that gas hydrates fill all the available pores in the sediments, thus over-predicting the CH_4 encaged in the reservoirs. Later, active drilling operations in hydrate sediments in the mid-1990s, with hydrate core samples and logs, suggested that a small fraction of the rock porosity mainly contains gas hydrates. However, an exception is normally observed when the formation has very high permeability and coarse-grained sands.

According to Boswell and Collett (2011), a relatively close prediction of gas hydrate is 3 × 1015 m^3. This value is estimated based on extensive review research estimates and given the data gathered through drilling operations of CH_4 hydrate gas in place in the world's gas hydrate reserves. This value correlates to about 1500 gigatons (Gt or 1015 g) or about 2.0 million Tg (1012 g) of C in CH_4. A recent prediction made by Dickens (2011) is similar to the estimation of Kvenvolden (1988), which is about 8.3 times greater than the estimation of Boswell and Collett (2011). It is interesting to note that the world CH_4 hydrate in-place is still not well understood with variations and inconsistencies in predictions.

5.2 Climate Change and CH_4 Hydrates

The increase in temperature and decrease in pressure are the main factors responsible for gas hydrate destabilization. Herein, we explore the impact of gas hydrate instability on the climate event. The temperature and pressure (rise in sea level) of the air and ocean are increased by global warming. Generally, the effect of relatively high temperature on gas hydrate destabilization around the phase boundary conditions is stronger than that of rising sea level. However, in an elastic sediment environment, the rising sea level with increasing pressure causes more gas hydrate destabilization relatively instantaneous.

Contrary, in the permafrost and seafloor environment, the effect of temperature changes on gas hydrates destabilization might occur very slow for several years depending on the thermal diffusivity and sediment thickness. This delay may result in the release of more free CH_4 in the atmosphere over a wide range of time due to climate perturbations. There have been gas hydrate depressurization impacts which correspond to about 1 km since 50 Ma. This impact has resulted in thawing the ice sheets that might get to the depths greater than the overall sea-level range (about 300 m) (Miller et al. 2005). This thawing of ice sheets might be responsible for the basis of gas hydrate dissociation in deglacial cycles. Warming temperatures is the next hydrate dissociation parameter responsible for dissociation. The climate-based effect on hydrate reservoirs is very direct and relatively static during the times of stability in the climate. Thus, there is a continuous melting of the gas hydrate present in the hydrate stability zone as a result of the normal sedimentation and pressure and temperature changes to depth (Dickens 2011). Also, the effect of previous climate change events can dictate the way gas hydrate reservoir may adapt to future climate change.

However, the estimated changes observed by past climate actions are very negligible compared with anthropogenically driven global warming that is affecting the stability of deep ocean hydrates. In addition, gas hydrate dissociation is a very slow reaction and not instantaneous just on simple changes in pressure or temperature conditions in the sediments in the gas hydrate stability phase conditions. Interestingly, gas hydrate has an internal process of self-regulating its dissociation behaviour. This is mainly controlled by the endothermic nature of hydrate formation (Circone et al. 2005). Thus, providing an endothermic heat of reaction (~439 Jg^{-1} of CH_4hydrate) (Gupta et al. 2008) prevents the fast melting of hydrates and renders the melting mechanism a self-regulating process.

5.3 Methane Carbon Sink Stability and Dissociation

In the process of CH_4 freed from gas hydrates, a very minimal amount is exposed to the atmosphere due to the presence of chemical, physical, and biological sinks. These sinks inhibit the quantity of CH_4 that reaches the atmosphere. The activities of these sinks are so powerful that there are very limited places on the Earth where hydrate dissociation could free a significant amount of CH_4 to the atmosphere (Ruppel and Kessler 2017).

Biochemical sinks are the most dominants in shallow marine sedimentary environments. The biochemical sinks are mainly driven by the principle of anaerobic oxidation of methane (AOM). A certain group of microbes is usually responsible for this process (Knittel and Boetius 2009). They also take part in the sulphate reduction process, especially in the provinces which are dominantly diffusive and have no extra hydrocarbon sources. The SRZ, known as sulphate reduction zone, is around a few centimetres to metres beneath the floor of the sea, with a deeper SRZ similar to the lower upward CH_4 flux (Borowski et al. 1997). The group of microbial agents that is responsible for anaerobic oxidation of CH_4 (Boetius et al. 2000) is known as biofilter that avoids the upward movement of CH_4 from getting to the seafloor and, finally, dissolves in the ocean. According to Reeburgh (2007), AOM consumes about 80–90% of the calculated 400 Tg/year CH_4 at the SRZ through an upward movement via sediments. Also, the presence of physical properties such as traps, low permeability, and hydrate and/or gas-saturated sediments may also prevent the migration of dissociated CH_4 to the atmosphere. Unlike the anaerobic oxidation of CH_4, the physical characteristics of marine sediments do not change or convert the CH_4 in the way. They only prevent the released CH_4 from interacting with the ocean-atmosphere system for thousands of years.

In the case of the water column (on the seafloor), CH_4 sinks are based on the solubility and concentration of CH_4 in seawater. The concentration of CH_4 in seawaters is very low that the gas diffuses very fast from the released CH_4 gas bubbles owing to its release from gas hydrates sediments. Interestingly, CH_4 is usually replaced by nitrogen and oxygen during this bubble-stripping process. When CH_4 is dissolved in the seawaters, the CH_4 may be able to reach the atmosphere by gas exchange mechanism. However, the dissolved CH_4 could remain in the waters for centuries in deeper waters based on the nature of ocean circulation and the depth.

In addition, anaerobic microbial oxidation could also further act on the dissolved CH_4 and limit its migration to the atmosphere. On the other hand, the gas hydrate present in the cold region terrestrial known as permafrost is also been under constant sink processed. In the case where the gas hydrate is in a deeply buried permafrost region (Ruppel 2015), the migration of CH_4 to the atmosphere may face microbial sinks. This ensures aerobic and anaerobic oxidation of CH_4 in permafrost. The CH_4 oxidation relay on the type of marine sediments (Lee et al. 2012) and the type of physical sinks present. Pore-filling ice is a special kind of physical barrier in high-latitude environments that can capture dissociated CH_4 from hydrates in the permafrost.

5.4 The Sensitivity of Methane Hydrate to the Amount of Methane in the Atmosphere

The amount of CH_4 in the atmosphere is believed to vary due to the amount of CH_4 released to the atmosphere from CH_4 hydrates. However, the dependence or association of the variation of CH_4 in the atmosphere to the melting of CH_4 hydrates is an ongoing debate and ambiguous topic of debate. Table 1 represents the estimated amount of C released in the atmosphere for gas hydrate sources. Interestingly, the rising association of CH_4 hydrate dissociation to climate change is at higher alarms. This CH_4 hydrate dissociation might be motivated by global warming which may produce positive climate feedback that could increase anthropogenic warming (Harvey and Huang 1995).

The elevation of greenhouse gases in the atmosphere causes high temperatures in the atmosphere, oceans, and permafrost (Dickens 2011; Meena et al. 2020). This increasing temperature in marine and permafrost regions causes the dissociation of CH_4 hydrates, thus reducing the quantity of hydrates. The increasing temperatures in these regions are time dependant and may last for a very long period, depending on the type of region. However, areas such as the permafrost are very prone to huge warming exposure. According to Dickens (2011), the amount of CH_4 hydrates in the gas hydrate stability zone of the Paleocene-Eocene Thermal Maximum (PETM) is at an elevated temperature of 5 °C. Similarly, a model by Buffett and Archer (2004) estimated the quantity of CH_4 hydrates when temperatures increase in marine environments. They reported that the quantity of CH_4 hydrate reduced in the presence of increasing temperature. About a 15% reduction of CH_4 hydrate could be observed when marine temperature increases by 3 °C at steady-state conditions with no time dependence factor.

Table 1 Carbon released in the atmosphere from hydrate sources

Authors	C ($TgCH_4$ $year^{-1}$)	Source
Kvenvolden (1988)	5	Hydrates
Fung et al. (1991)	5	
Wuebbles and Hayhoe (2002)		
Judd (2000)		
Wang et al. (2004)	4	
Denman and Brasseur (2016)	6	

CH_4 hydrate in the Earth is believed to be well insulated, which guarantees a very slow CH_4 hydrate dissociation rate, which could last for millennia periods Archer (2007). A 1 °C increase in 100 m depth water level could be achieved in 2000 years with a 2 °C anomaly. The heat in the CH_4 hydrate dissociation process further reduces due to the endothermic reaction in the dissociation process. The impact of sea level (pressure) and seafloor temperature on CH_4 hydrate reservoirs in the gas hydrate stability zone has been studied by several authors (Katz et al. 2001; Dickens 2003). Also, the effect of CH_4 dissociation on the climate has been modelled to calculate the variation in the gas hydrate stability zone. These studies were performed using climate models including time-dependent parameters. These models show that the warming in the continental margins is very high than the global warming. It is also proven that more than 50% of the CH_4 hydrate in the gas hydrate stability zone happened during 5000 years before the C dioxide elevation in the atmosphere. The reduction in the CH_4 hydrate mostly happened in shallow waters with mid to high latitudes in the sea ice, with an additional disturbance effect arising from the seafloor thermal diffusivity.

The dissociation of CH_4 hydrates in the seafloor will only occur when there is a significant temperature increase through the bottoms of the gas hydrate stability zone. Fig. 8 shows the dissociation of CH_4 hydrate in a shallow and deep marine environment. CH_4 hydrate dissociation occurs at both the upper and lower part of the gas hydrate dissociation zone of the shallow marine environments. However, in the deep marine zone, the dissociation happens at the lower part of the gas hydrate stability zone, as shown in Fig. 8a and b, respectively.

The use of simulation software such as TOUGH+HYDRATE has been employed to model the estimated potentials of frozen CH_4 C dissociation with regard to drilling in the offshore environment. The model predictions are controlled by analysing the difference in the pressure and temperature, coupled with the fluid movement effect on the downward sediments in the gas hydrate stability zones. This model results in the understanding of the process by which CH_4 can migrate upward.

According to the prediction simulation by Panel and Change (2008), the Northern Hemisphere (50°N) records the most temperature elevation effect. The simulation was concluded using data from the fourth assessment report of the IPCC meeting. The main aim was to study and estimate the amount of CH_4 released from frozen CH_4 carbon. His model assumed that the condition causing the presence of frozen CH_4C (CH_4hydrates) is the pressure (depth) and temperature. Thus, based on the temperature variation, he predicted that the amount of CH_4 released from the destabilizing temperature fluctuations at the ocean gas hydrate stability base is about 560–2140 Tg of CH_4 per year. However, based on the amount of CH_4 moving to the atmosphere with a huge gas seepage rate of 1%, the observed CH_4 flux was decreased to 5–21 Tg of CH_4 per year (Mau et al. 2007).

However, it's worth noting that the CH_4 seepage from frozen CH_4 C in the seabed to the atmosphere is highly inaccurate with about 30% prediction errors (uncertainties). All the present models have trial form including the period (time scale) of temperature changes from the seafloor into the bottom of the gas hydrate stability zone sediments. Other factors that have not been well factored in the

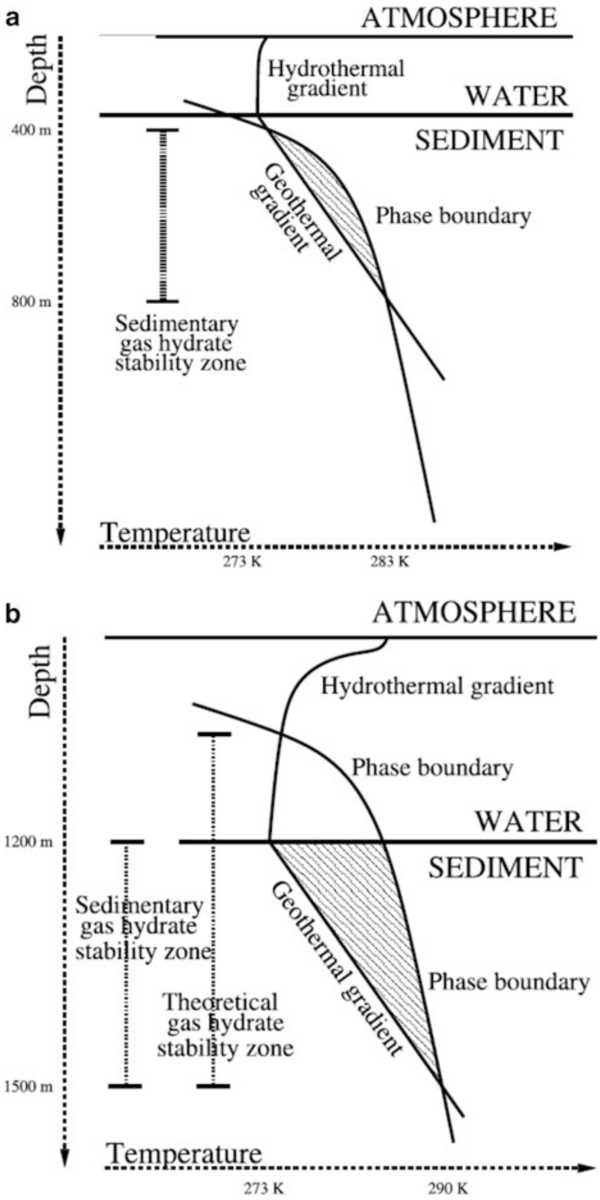


Fig. 8 Gas hydrate dissociation in the gas hydrate stability zone; (**a**) shallow marine; (**b**) deep marine (Connor et al. 2010)

existing models are the CH_4 hydrate depth and/or global geographical occurrence. Westbrook et al. (2009) reported that the increase in seawater temperature by 1 °C over the past three decades has shown the release of CH_4 gas at the seabed of the West Spitsbergen. This demonstrates the relationship between seawater bottom temperature variation and the dissociation of CH_4 hydrates in our present days. However, some of the migrated gas to the seawaters are the free gas which is normally associated beneath the gas hydrate stability zone.

6 Application of Frozen Carbon and Future Perspectives

CH_4 hydrate or frozen C has been a great threat to climate change activist, and there are serious studies to develop ways in understanding and preventing the release of CH_4 in the atmosphere from gas hydrate sediments and related areas. Interestingly, CH_4 hydrates or frozen C may as well be a good method for tackling global warming through storing CO_2 and producing CH_4 (clean energy) for future use. Since fossil fuels produce lots of carbons in the atmosphere, there are currently active research on developing potential methods for producing CH_4 from gas hydrate reservoirs around the globe. Depressurization, heating, and the use of inhibitors are the major methods that have been explored. Other challenges related to the stability of the reservoir have been major concerns. However, the proposed solution to such is the injection of CO_2 into the hydrate reservoir to swap with CH_4 as an energy source. This concept is still under research and could permanently tackle global CO_2 storage challenges.

A report from the European Union of Geosciences, European Geophysical Society, and the American Geological Union suggests the potential production of large amounts of CH_4 from deep marine frozen C in commercial quantities. It was previously believed that the amount of CH_4 trapped in the permafrost areas is more economically advantageous for production than in the deep marine ocean. However, the reports from the Leg 204 have proven otherwise. Thus, indicating that the amount of CH_4 energy stored in deep marine sediments as hydrates are in higher magnitudes greater than in the permafrost hydrates. In addition, the accessible CH_4 hydrate production recoverability is more in deep marine oceans than in the permafrost regions.

It is worth noting that reservoir gas recovery models based on finite-difference have shown that the CH_4 production rates greater than 500,000 standard cubic meters (0.1 MPa and 289 K) per day would be suitable for the economic viability of the CH_4 hydrate recovery methods.

Thus, all the current testing methods are not very strong to produce the minimum required CH_4 recovery rate. To produce more CH_4 for the frozen CH_4 C in the permafrost regions, more focus should be pushed towards the hydrate present to the adjacent of the gas reservoir. This would cause more CH_4 recovery due to the free gas in the gas reservoir, which will cause a decrease in the hydrate stability pressure and result in the dissociation of the CH_4 from the frozen CH_4 C. The production of CH_4 from the permafrost CH_4 hydrate is very expensive, though it is feasible. However, actions have been taken by the USA and Japan and other countries to begin CH_4 hydrate production with some successful well testing operations, especially in China and Japan.

7 Conclusions

In conclusion, hydrates are dissociating in some areas of the permafrost and marine sediments which is likely associated with the changing climate and warming globe. However, the fear of the release of OC trapped in frozen form to the atmosphere is not significant. This is mainly due to chemical, biological, and physical C sink processes which mitigates the released/dissolved CH_4 to the atmosphere. In addition, the quantification of CH_4 hydrate deposition in the Earth is not well established in the global C cycle, thus requiring a better model to properly estimate its impact on the climate. Interestingly, these CH_4 hydrates are potential candidates for future clean energy production and C dioxide storage to combat climate change.

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How Soil Organic Carbon Fractions Affect N_2O Emissions in a Long-Term Integrated Crop-Livestock System: A Case Study

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Abstract

The nitrous oxide (N_2O) emissions in agricultural systems are influenced by edaphoclimatic conditions, and the availability of soil organic matter (SOM) is a key factor in this process. Understand the relationship between SOM fractions

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and N_2O emissions in cultivated soils is fundamental to the sustainable management of tropical soils. However, this relationship remains unclear. The objective of this study was to evaluate the accumulation of labile and stable fractions of SOM and their relations with N_2O emissions in a 24-year field study that represents farm conditions in the Cerrado region. The following hypotheses were considered: (i) conservation systems protect SOM, avoiding its rapid decomposition and, consequently, reducing losses of N_2O to the atmosphere; (ii) conservation systems favor the increase of labile and stable fractions of SOM, which has the effect of reducing the N_2O emission in the soil. The following land-use systems were assessed: no-tillage with integrated crop-livestock system (NT1); no-tillage with continuous cropping (NT2); and conventional system (CT). An area of native vegetation of Cerrado was used as a reference. Nitrous oxide emissions were quantified over a period of 509 days, covering two agricultural years with soybean crop followed by sorghum and corn as a second crop in 2014/2015 and 2015/2016 agricultural years, respectively. Soil carbon fractions (labile and stable) and carbon in different classes of soil aggregates were also determined. The cumulative N_2O emissions were larger in CT, intermediate in NT systems, and smaller in the Cerrado area. Among the agricultural systems, lower cumulative N_2O emissions were observed in NT1, because of the greatest buildup of carbon in its most stable fractions and occluded in aggregates. From PCA results, it is possible to conclude that aggregation is a key factor that correlates with N_2O emissions from soil. Thus, NT1 showed the largest average diameter of aggregates and presented the lowest N_2O emissions among agroecosystems. Although the conservation systems show a greater microbial population, stable fractions of carbon are predominant, which decreases availability for the soil microbiota, which justifies lower rates of SOM mineralization and, consequently, the lowest N_2O emissions.

Keywords

Soil organic matter · Carbon stability · No tillage · Greenhouse gases · Brazilian Cerrado

Abbreviations

N_2O	Nitrous oxide
SOM	Soil organic matter
NT1	No-tillage with crop-livestock in the pasture phase
NT2	No-tillage with crop-livestock in the crop phase
CT	Conventional tillage
CER	Cerrado area
PCA	Principal component analysis
GHG	Greenhouse gases
CO_2	Carbon dioxide
CH_4	Methane

IPCC	International panel on climate change
COP	Conference of the parties
iNDC	Intended Nationally Determined Contributions
CLS	Crop-livestock integrated system
C	Carbon
N	Nitrogen
C:N	Carbon nitrogen ratio
TOC	Total carbon
TN	Total nitrogen
LC	Labile carbon
ADFS	Air-dried fine soil
POC	Particulate organic carbon
HA	Humic acid
FA	Fulvic acid
HI	Humification index
HUM	Humin
IC	Inert carbon
MWD	Mean weight diameter
MBC	Microbial biomass carbon
C-MACRO	Carbon in macroaggregates
C-MICRO	Carbon in microaggregates
N-MACRO	Nitrogen in macroaggregates
N-MICRO	Nitrogen in microaggregates

1 Introduction

The discussions on global climate change and greenhouse gas emissions (GHG) took on significant proportions during the 1990s and early 2000s due to increased anthropic concentrations of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) in the atmosphere. This discussion was highlighted after the publication of the IPCC report (2018) which pointed to the urgent reduction in GHG emissions to contain the average temperature increase on the planet below 2 °C. The trend of increasing GHG concentrations is expected to continue in the coming decades, and, if urgent measures are not adopted, it should be twice as high until 2050 when compared to the 1990s (Meinshausen et al. 2009). This increase is a result of both industrial development and food production with the expansion of the agricultural area in countries where the consumption of nitrogen fertilizers is growing and intensive (Smith et al. 2007). The need to increase food production has led to an increase in anthropogenic GHG emissions into the atmosphere because of the increased use of synthetic fertilizers in agriculture and livestock. In the case of N_2O, the agricultural sector is the main responsible for its emissions to the atmosphere, as a consequence of the oxidation of organic matter and complex microbial processes associated with the management practices of plant residues (Carvalho et al. 2016; Santos et al. 2016; Sato et al. 2017; Figueiredo et al. 2018).

During COP 21 in Paris, the Brazilian government, through its Intended Nationally Determined Contributions (INDC), pledged to reduce by 43% the emission greenhouse gases (GHG) in Brazil until 2030. In the agricultural and livestock sector, among other nations, the government established, as its goal, to recover 15 million hectares degraded pastures and to incorporate 5 million hectares of crop-livestock integrated systems (CLS) (Brazil 2015).

The integrated cropping systems are considered more efficient in recycling soil nutrients (Salton et al. 2014), as they improve soil quality (Salton et al. 2014), increase diversity of the fauna (Marchão et al. 2009a), and represent efficient carbon drainage, contributing to the mitigation of GHG emissions (Buller et al. 2015).

Among the GHGs, nitrous oxide (N_2O) gained notoriety for being potentially more harmful than CO_2, because of its greater warming capacity and longer time of permanence in the atmosphere, approximately 100 years. In Latin America, Brazil is the largest emitter of N_2O (Bustamante et al. 2014). The N_2O emission from soil in agricultural systems is affected by several factors such as content of water, which favors anaerobiosis processes (Butterbach-Ball et al. 2013); the soil acidity, which alters the nitrification and denitrification processes (Martins et al. 2015); N fertilizers, which affect the N availability (Metay et al. 2011; Martins et al. 2015); the tillage system, which changes the soil porosity and microbial communities (Bayer et al. 2015); the animal excrements (Buller et al. 2015); and the C:N ratio of SOM, which favor soil microorganisms (Bhattacharyya et al. 2013; Meena et al. 2020b).

Land-use systems may build up stable SOM from plant residues, which alter the dynamics of denitrification and, consequently, the N_2O production (Miller et al. 2008). However, the manner in which C accumulates in the soil in the different agricultural systems is variable, influencing its availability and the N dynamics, in function of the C:N ratio, and therefore in the N_2O released from the soil (Kong et al. 2009).

The greatest buildup of C in its recalcitrant fractions is normally associated to a greater degree of stability of SOM (Plaza-Bonilla et al. 2014). The chemical and physical fractionation techniques of SOM have been developed and supplied information on stability and location of SOM fractions in soil compartments. The C fractions indicate sensibility to alterations in soil management, whether they are short-term, as in labile carbon and microbial biomass C (Guimarães et al. 2013; Meena et al. 2018) or long-term, as in organic mineral-associated C (Trigalet et al. 2014).

The accumulation of different fractions of organic C is influenced by climatic conditions and soil management (Bayer et al. 2011). In contrast to conventional tillage with intensive plough, conservation practices as no-till associated with the integration of crops lead to maintain or increase SOM, reducing GHG emissions (Six et al. 2004; Buller et al. 2015).

The ability to protect and stabilize soil C depends on the management practices adopted and on the soil's intrinsic characteristics (Bayer et al. 2011). In Oxisols, chemical stabilization is highlighted by the strong organomineral interaction (Six et al. 2004). Physical protection (formation of aggregates), on the other hand, is considered as a stabilization mechanism that predominates in conservation systems in temperate soils and in most tropical soils (Six et al. 2004; Conceição et al. 2008). The C accumulation in its most stable forms is associated with a higher degree of SOM stabilization (Six et al. 2002; Plaza et al. 2013; Plaza-Bonilla et al. 2014), resulting from the less exposure of SOM to the mineralization process, due to the more difficult access of decomposing microorganisms (Jahangir et al. 2014; Meena and Lal 2018).

The soil aggregation and its dynamics are fundamental for the SOM stabilization (Plaza et al. 2013). According to the aggregate formation process proposed by Golchin et al. (1994), fresh plant material incorporated into the soil is colonized by microorganisms and encrusted by primary particles through the binding action of microbial agents (e.g., mucilage and polysaccharides), thus forming macroaggregate. Over time, fresh plant material within macroaggregates is selectively decomposed leaving recalcitrant vegetable structural materials, which are coated with microbial metabolites and mineral particles to form stable microaggregates. The process of formation of macroaggregates is dependent on the continuous supply of C to the soil and, therefore, is regulated by the agricultural system (Bayer et al. 2011). Management systems that favor the intense supply of C, therefore, will favor the formation of aggregates and, consequently, higher soil C stocks with greater SOM stability. In no-tillage systems, the C input is more protected than those from conventional till because macroaggregates have a longer residence time. In addition, crop rotation favors a greater C supply in intra-aggregates (Zotarelli et al. 2007). Thus, the formation of macroaggregates is a key process for C sequestration and GHG mitigation (Chung et al. 2008; Meena et al. 2020a).

Considering that 98% of the total N of the soil is in organic forms (Stevenson 1994), and the availability and dynamics of N are influenced by the C:N ratio of the soil (Kong et al. 2009), the C fractions can affect the N_2O emissions. According to Miller et al. (2008), the availability of C in the soil, when coming from less complex sources such as glucose, will favor the production of N_2O. In addition, agricultural systems with more complex C sources, from plant residues with a higher C:N ratio, affect the rates of nitrification and denitrification, influencing the production of N_2O by the soil (Dendooven et al. 1996; Miller et al. 2008).

In a study in California, Kong et al. (2009) concluded that conventional till presents higher N conversion and incorporation in less stable silt and clay fractions, which provides greater N_2O flows. In Brazil, few studies correlate N_2O emissions with different fractions of SOM in agricultural systems. The greatest emphasis was given in soil C and N stocks (Coutinho et al. 2010; Bayer et al. 2015, 2016) and labile fractions such as microbial biomass C (Carvalho et al. 2017) and labile C (Carmo et al. 2005). Furthermore, in long-term experiments, SOM evaluation consider only the total C content which does not express the changes resulting from the management systems (Figueiredo et al. 2013). Additionally, it is relevant to explore the role of SOM fractions from different agroecosystems and their relationship with N_2O emissions.

In the Brazilian Cerrado, various studies demonstrated that N_2O emission is lower in native areas in comparison to agricultural systems, even though there is a greater content of organic carbon (Santos et al. 2016; Carvalho et al. 2017; Sato et al. 2017, 2019). However, land-use systems that are capable of balancing the increase of SOM content, with greater availability of N, without increasing the N_2O emissions in the atmosphere, are still scarce. Kong et al. (2009) noticed that the conventional system not only showed the fastest N turnover and more fertilizer-N incorporation into the less stable silt-and-clay fraction, but also the highest N_2O fluxes among the three assessed cropping systems. In Brazil, studies that correlate the N_2O flow to the different SOM fractions in land-use systems are rare.

From these results, we elaborated the hypothesis that the buildup of C in stable fractions of SOM, with greater degree of physical and chemical protection, would provoke smaller N_2O emissions. Additionally, the comprehension of the role of SOM fractions resulting from land-use practices on N_2O emissions is crucial for GHG mitigating. Therefore, the objective of this study was to evaluate the accumulation of SOM fractions and their relation to the N_2O emissions from the soil in a 24-year field trial in the Cerrado region.

2 Material and Methods

2.1 Study Site

The field trial was conducted at the experimental area located at latitude 15°39′ S, longitude 47°44′ W, and elevation of 1200 m, in Planaltina, DF, Brazil. The regional climate is classified as tropical savanna-Aw (Köppen classification), with a rainy season from October to March and a dry season from April to September. The soil was classified as typical Oxisol and had 610.5 g kg^{-1}, 79.5 g kg^{-1}, and 309 g kg^{-1} of clay, silt, and sand, respectively. Details on soil mineralogy are showed in Marchão et al. (2009b). Soil chemical attributes are presented in Table 1.

The field experiment was setup in 1991, with four replicates. Three land-use systems were assessed: (1) CT, continuous cropping with conventional tillage in the off-season (without grasses as cover crops); (2) NT1, no-tillage with crop-livestock system in the pasture phase with *Brachiaria brizantha* cv. Piatã; and (3) NT2, no-tillage in continuous cropping with *Brachiaria brizantha* cv. Piatã as cover crop and sorghum as a main crop (without off-season cattle). An adjacent native Cerrado vegetation characterized as typical savanna was studied as a reference of natural conditions. Figure 1 shows the sequence of operations and cropping performed in the experimental area over the 24 years. Details on history of land-use systems were comprehensively explained in Sato et al. (2019).

2.2 Soil Analysis and Gas Sampling

Soil samples (0–20 cm) were collected in October 2013, 20 days following soy planting, which preceded the sorghum (2013–2014 crop). In each area, four samples were collected. Each soil sample was composed of five sub-samples. After

Table 1 Soil chemical properties of the experimental area

		Al	Ca	H+Al	Mg	K	P	
Land-use system	Layer (cm)	(cmol$_c$ dm^{-3})				(mg dm^{-3})		pH
NT2	0–5	0.02 ± 0.0	3.97 ± 0.3	4.65 ± 0.7	1.06 ± 0.1	131.00 ± 44.1	14.41 ± 3.8	6.05 ± 0.2
	5–10	0.06 ± 0.0	2.04 ± 0.2	6.02 ± 0.9	0.50 ± 0.1	42.50 ± 25.0	9.00 ± 5.7	5.48 ± 0.2
	10–20	0.31 ± 0.1	0.69 ± 0.3	7.40 ± 0.6	0.18 ± 0.0	26.75 ± 5.6	3.06 ± 1.9	4.76 ± 0.1
	20–30	0.29 ± 0.1	0.58 ± 0.3	6.98 ± 0.6	0.15 ± 0.0	30.50 ± 3.3	2.63 ± 1.3	4.73 ± 0.0
CT	0–5	0.22 ± 0.1	1.31 ± 0.2	7.27 ± 0.8	0.20 ± 0.1	163.00 ± 57.7	8.59 ± 4.3	5.00 ± 0.2
	5–10	0.09 ± 0.1	2.18 ± 0.6	6.59 ± 0.1	0.36 ± 0.2	57.25 ± 26.4	7.92 ± 3.9	5.28 ± 0.2
	10–20	0.15 ± 0.0	1.27 ± 0.3	6.31 ± 0.5	0.26 ± 0.1	41.50 ± 10.6	2.35 ± 0.9	5.09 ± 0.1
	20–30	0.15 ± 0.1	1.08 ± 0.6	5.63 ± 0.2	0.23 ± 0.1	46.00 ± 9.4	1.58 ± 0.2	4.94 ± 0.1
NT1	0–5	0.05 ± 0.0	2.52 ± 0.2	5.40 ± 0.2	0.91 ± 0.2	123.00 ± 94.6	4.70 ± 2.4	5.60 ± 0.8
	5–10	0.14 ± 0.1	1.36 ± 0.3	5.82 ± 0.4	0.43 ± 0.1	48.75 ± 40.2	6.47 ± 5.6	5.22 ± 0.2
	10–20	0.19 ± 0.1	0.99 ± 0.3	5.87 ± 0.5	0.30 ± 0.1	21.50 ± 4.5	1.74 ± 0.3	4.98 ± 0.1
	20–30	0.19 ± 0.1	0.97 ± 0.1	5.73 ± 0.7	0.30 ± 0.1	20.00 ± 4.5	1.09 ± 0.2	5.03 ± 0.2
CER	0–5	0.65 ± 0.2	0.70 ± 0.3	10.22 ± 1.2	0.42 ± 0.2	74.00 ± 21.4	2.01 ± 0.2	4.88 ± 0.1
	5–10	0.71 ± 0.2	0.15 ± 0.2	8.54 ± 0.3	0.13 ± 0.2	44.00 ± 15.9	1.41 ± 0.2	4.74 ± 0.3
	10–20	0.46 ± 0.1	0.05 ± 0.1	7.16 ± 0.3	0.06 ± 0.1	31.00 ± 15.8	1.25 ± 0.1	4.91 ± 0.3
	20–30	0.34 ± 0.1	0.01 ± 0.0	6.24 ± 0.3	0.03 ± 0.0	22.50 ± 6.4	1.19 ± 0.1	4.98 ± 0.3

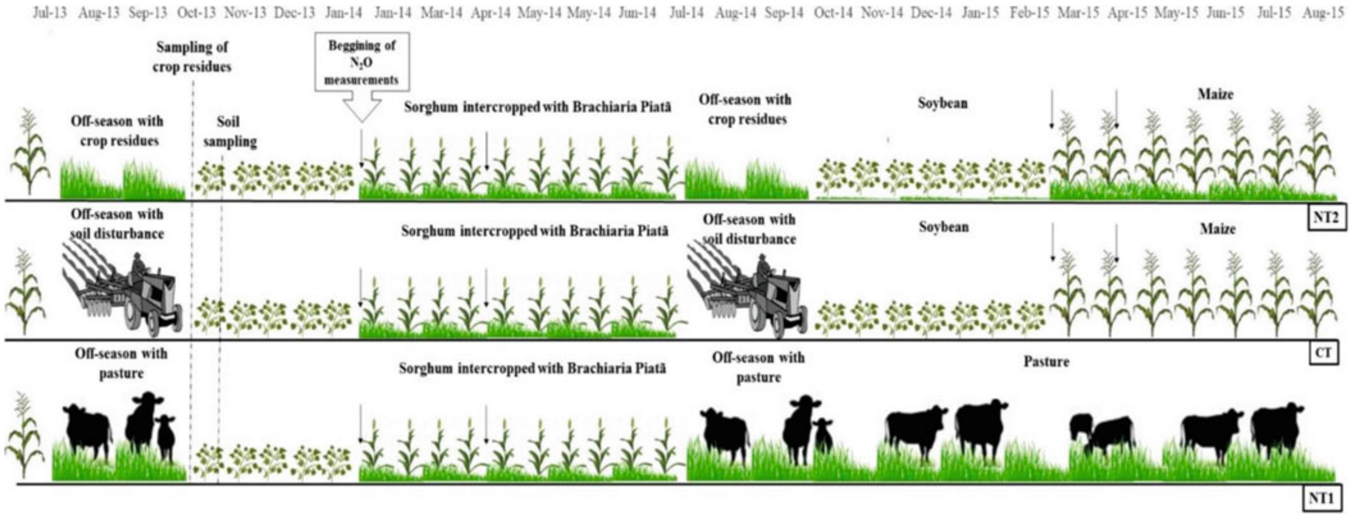

Fig. 1 Schematic representation of the experimental area and all operations performed along the cropping seasons

collection, the samples were air-dried and sieved (<2 mm). Background information on soil chemical analysis is available in our previous work (Sato et al. 2019).

2.2.1 Total Carbon and Total Nitrogen

The total N and C contents were determined using an elemental analyzer (Finnigan MAT, Bremen, Germany).

2.2.2 Labile Carbon

The labile C (LC) was considered as C susceptible to oxidation by a solution of $KMnO_4$ 0.033 mol L^{-1} (Blair et al. 1995). The samples were analyzed in spectrophotometer (565 nm).

2.2.3 Physical Granulometric Fractioning

Air-dried fine soil (ADFS) samples (20 g) were submitted to the physical granulometric fractioning (Cambardella and Elliot 1992). The C was determined through dry combustion in a Perkin Elmer Series II CHNS/O 2400 analyzer. The mineral-associated organic C (MOC) was obtained by the difference between TOC and particulate organic C (POC).

2.2.4 Microbial Biomass Carbon

The microbial biomass C (MBC) was determined through the irradiation-extraction method (Islam and Weil 1998), using 0.5 mol L^{-1} potassium sulfate as an extractor. The carbon quantification was determined by the method of oxi-reduction with 0.066 mol L^{-1} potassium dichromate and 0.033 mol L^{-1} ammonium iron(II) sulfate (Mohr's salt). The amount of MBC was estimated by the difference between C extracted from irradiated and non-irradiated soil samples (Mendonça and Matos 2005).

2.2.5 Chemical Fractioning of Soil Organic Matter

The differential solubility technique was used for the chemical fractioning of the SOM using 0.1 mol L^{-1} of NaOH (proportion of 1:20) as an extractor (Mendonça and Matos 2005). The following fractions were obtained-humic acid HA-C; fulvic acid FA-C; and humin HUM-C. The humification index (HI) was estimated as follows $\mathrm{HI} = [(\mathrm{HA\text{-}C} + \mathrm{FA\text{-}C} + \mathrm{HUM\text{-}C})/\mathrm{TOC}] \times 100$.

2.2.6 Inert Carbon

Inert C was considered the fraction of SOM which remains after oxidation with hydrogen peroxide (H_2O_2) at 30% (v/v), according to Jackson (1958).

2.2.7 Carbon and Nitrogen Contents in Macro- and Microaggregates

The soil samples were collected from mini-trenches, following the methodology proposed by Madari et al. (2005), for quantification of C in different classes of aggregates that are stable in water. In each installment, mini-trenches were dug in four random locations. These samples were sifted, still in the field, in a 19 mm mesh sieve with 210 mm in diameter, with the intention of preserving the natural characteristics of the soil. After sifting in the field, the material was stored in plastic recipients and sent to the laboratory to be air-dried in a shady location. Subsequently, the samples underwent water aggregate stability analysis in a vertical oscillation shaker (Yoder sieve shaker), according to the method proposed by Embrapa (1997).

After separation of aggregate classes, two classes were utilized for the quantification of total C in macroaggregates (>25 mm) and microaggregates (<25 smm). The mean weight diameter (MWD) of the aggregates was also calculated through the Kemper and Rosenau method (1986). To determine total C and N, the samples were grouped as macroaggregates and microaggregates. The quantification of C and N was carried out in an elemental analyzer in Soil Laboratory at Embrapa Cerrados.

2.3 Cumulative N_2O Emissions

N_2O fluxes measurements were performed 114 times from March 21, 2014, to August 12, 2015, over a period of 509 days (Fig. 1). The static chamber method was used (Alves et al. 2012).

The N_2O concentration was determined by gas chromatography (Trace GC Ultra, Thermo Scientific). Details on N_2O calculation are showed in Sato et al. (2019).

2.4 Statistical Analysis

The data were submitted to ANOVA, and the comparison of means was conducted with Tukey-Kramer test ($P < 0.05$) by using the GLIMMIX procedure of SAS. Descriptive statistical analyses were also performed for the attributes of SOM, and boxplots were used to the data display of each treatment.

A principal component analysis (PCA) was applied in a data matrix with 12 lines composed by 3 land-use systems and 4 repetitions per treatment and 16 columns comprising the organic matter attributes and cumulative N_2O emissions. The PCA was performed using XLSTAT software.

3 Results

3.1 Total Carbon and Nitrogen on Land-Use Systems

3.1.1 Total Carbon and Nitrogen

The TOC and TN contents are shown in Fig. 2. CER had the highest levels of TOC in soil (26.32 g kg^{-1}). The NT1 and NT2 systems presented an intermediary condition (25.31 and 24.53 g kg^{-1}, respectively). CT was the system that exhibited the lowest levels of TOC (19.81 g kg^{-1}), significantly different from the other land-use systems ($p < 0.05$).

The integrated system (NT1) had similar content of TN (1.58 g kg^{-1}) to the CER soil (1.50 g kg^{-1}) and larger than the CT and NT2 systems. The continuous crops

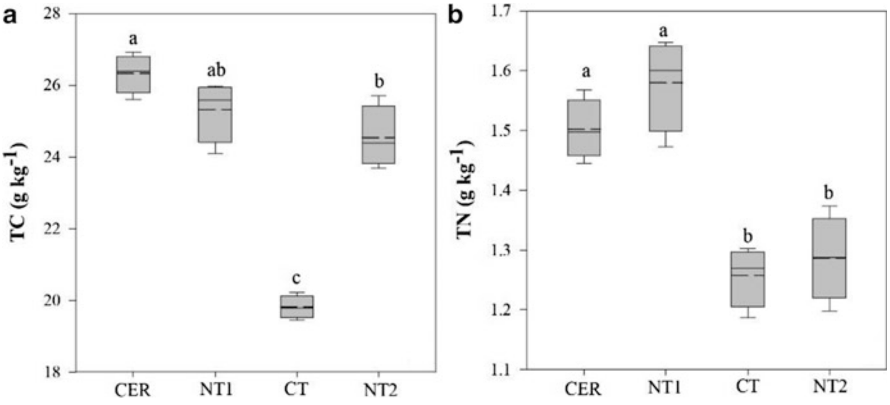

Fig. 2 (**a**) Total organic carbon (TOC) in soil; and (**b**), total nitrogen (TN) in soil submitted to different land-use system. Cerrado (CER); No-tillage with integrated crop-livestock (NT1); No-tillage with continuous cropping system (NT2); Continuous cropping system under annual heavy disc harrow (CT). Same letters within treatments indicate no difference (Tukey-Kramer; $p < 0.05$)

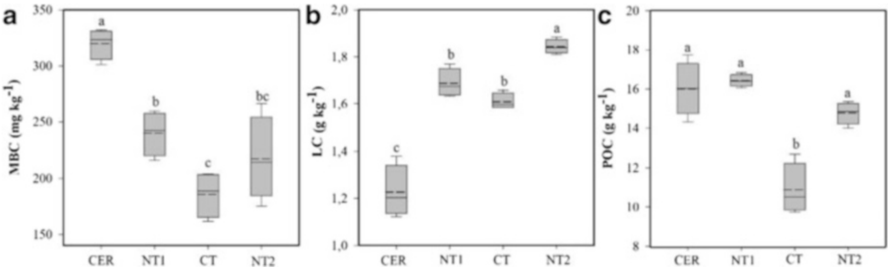

Fig. 3 (**a**) Microbial biomass carbon (MBC) in soil; (**b**). labile carbon (LC); and (**c**) particulate organic carbon (POC) in the different land-use systems. Descriptions of treatments are shown in the caption of Fig. 2. Same letters within treatments indicate no difference (Tukey-Kramer; $p < 0.05$)

were similar and presented the lowest levels of NT in the soil (1.26 g kg^{-1} in CT and 1.29 in NT2 g kg^{-1}).

3.1.2 Carbon Labile Fractions

The CER presented the highest levels of microbial biomass carbon (MBC) in the soil (320.13 mg kg^{-1}), the NT1 had intermediary levels (239.94 mg kg^{-1}), and the continuous cropping systems (NT2 and CT) had the lowest contents of MBC in the soil (Fig. 3a). Compared to the CER, the CT reduced the MBC in 42%, and NT1 reduced it in 25%.

Regarding the levels of LC (Fig. 3b), the CER soil presented the lowest levels (1.23 g kg^{-1}) compared to the cropping systems. There was no difference between the CT and NT1 ($p < 0.05$), with averages of 1.61 and 1.69 g kg^{-1}, respectively. The NT2 was the system with highest levels of POC in the soil (1.84 g kg^{-1}).

The highest levels of POC in the soil were observed in the NT1 (16.43 g kg^{-1}). In the CER soil, the POC showed a high coefficient of variation of 42%. Conventional system promoted the lowest value of POC (10.88 g kg^{-1}, on average) being different from the other agroecosystems and CER ($p < 0.05$).

3.1.3 Carbon Stable Fractions

The levels of carbon in humic fractions are shown in Fig. 4. The fulvic acid fraction (FA-C) in the soil did not present differences between the cropping systems and CER ($p < 0.05$). CER showed the lowest content of HA-C (3.03 g kg^{-1}).

The CER showed highest level of C in the humic fraction (HUM-C) (7.10 g kg^{-1}), being higher than the other agroecosystems ($p < 0.05$). The three agroecosystems had similar content of HUM-C. The CER soil presented the highest levels of MOC (18.26 g kg^{-1}). Compared to CER, on average, all agroecosystems decreased 50% of the MOC content.

With regard to the levels of inert carbon (IC) in the soil, the NT1 system showed the highest content (8.20 g kg^{-1}) and the CT the smallest content (5.48 g kg^{-1}), reducing in 22% the IC content in comparison to the CER soil. The CER had similar content of IC to CT.

The HA-C/FA-C ratio was not affected by agroecosystems ($p < 0.05$). The CT system presented the highest humification index (HI) (74% on average). The CER exhibited the smallest HI (53%), and the NT1 and NT2 systems exhibited intermediary values of 60% and 58%, respectively.

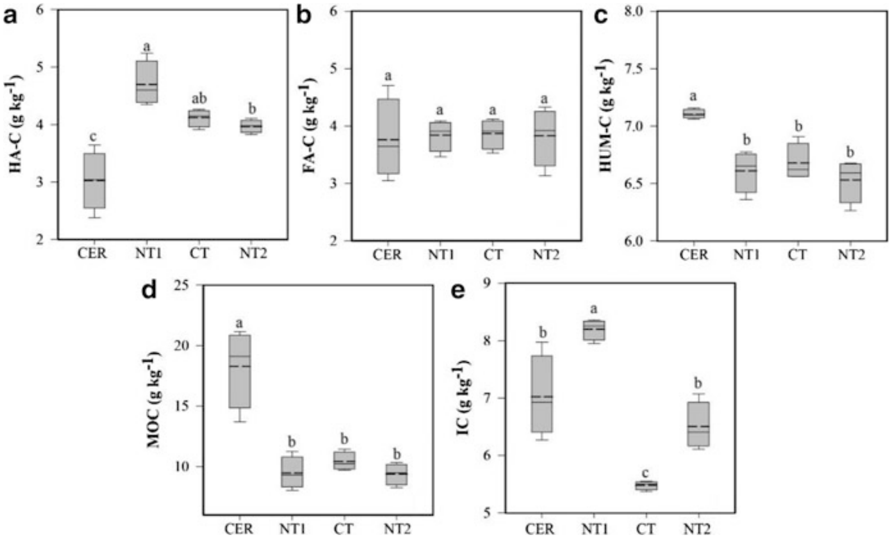

Fig. 4 (**a**) Fulvic acid (FA-C); (**b**) humic acid (HA-C); (**c**) humin (HUM-C) in soil; (**d**) mineral-associated organic carbon (MOC); (**e**) inert carbon (IC), in the different land-use systems. Descriptions of treatments are shown in the caption of Fig. 2. Same letters within treatments indicate no difference (Tukey-Kramer; $p < 0.05$)

3.1.4 Soil Aggregation, Carbon and Nitrogen Content in Macro and Microaggregates

NT2 presented in the Fig. 6 shows lowest levels of C in macroaggregates (C_{MACRO}) (20.71 g kg^{-1}) in the soil, 21% lower than the CER. Concerning the C in microaggregates (C_{MICRO}) in the soil, the NT1 showed the highest content (20.02 g kg^{-1}), with no differences between the other agroecosystems. The lowest content was found in the CER (17.34 g kg^{-1}).

The NT1 system exhibited the highest values of mean weight diameter (MWD), with average of 4.57 mm. The MWD of NT1 was 17% greater than the CER soil (3.90 mm). The continuous cropping showed a MWD value around 30–39% lower than the CER soil, with an average of 2.37 mm in CT and 2.75 mm in NT2.

With regard to the N content in soil aggregates, the highest content of N was found in the cropping systems soil, in both macroaggregates (N_{MACRO}) and microaggregates (N_{MICRO}). For the results, the CT exhibited a rate of N_{MACRO} (18.42 g kg^{-1}) 10% greater than the CER soil. NT2 had lowest N_{MACRO} content ($p < 0.05$). For the N_{MICRO} results, NT1 and NT2 showed higher contents than CER ($p < 0.05$).

3.2 Cumulative N_2O Emissions

Figure 7 shows the dynamics of the N_2O daily and cumulative fluxes for a period of a year and a half, which were correlated to the different C fractions in the soil (Fig. 8). The CT exhibited the highest fluxes of N_2O throughout a period of 509 days, with a cumulative emission of 4.56 kg ha^{-1}, while in the NT2 system the N_2O emission at the same period was 3.73 kg ha^{-1}. The NT1 had the lowest emission of N_2O from the soil (1.75 kg ha^{-1}). The CER had the lowest cumulative emission of N_2O (0.63 kg ha^{-1}), and the NT1 was similar to the reference area.

Two principal component analyses were performed. In the first, we considered all land-use systems including the Cerrado (Fig. 8a) and in the second only agricultural systems during the sorghum crop cycle were included (Fig. 8b).

The first PCA, performed with the data of SOM fractions and the N_2O accumulated in 509 days, revealed that the two first factors explained 69.71% of total data variability, of which 41.64% were explained by factor 1 and 28.07% by factor 2.

It is possible to observe that the factor 1 is associated with a SOM gradient in the areas, while factor 2 is related to soil aggregation and structure. Factor 1 is primarily correlated to the MBC, MOC, and HUM-C variables with positive eigenvectors and to N_2O and LC with negative eigenvectors. Factor 2 was correlated to the MWD, C_{MICRO}, N_{MICRO}, and POC variables, all of them with positive eigenvectors. A cluster of the areas may be observed in relation to the quadrants of the biplot. The cumulative N_2O emission was grouped in the quadrant of the CT, the opposite of the NT1 system, which correlated to the soil aggregation (MWD) and total C and N contents.

In the second PCA, with exception of the data from the Cerrado area and considering only N_2O cumulative emissions from agricultural systems during the sorghum cycle, the results revealed that the two first factors explained 66.09% of total data variability, of which 46.20% were explained by factor 1 and 19.89% by factor 2. The factor 1 clearly shows a positive relation between N_2O and carbon stable fractions, represented by the humification index (HI). In an opposite way, one can see a higher distance between N_2O and labile carbon fractions. Continuous crop under conventional tillage was the systems that better correlates with low contents of labile fractions and N_2O emissions.

4 Discussion

4.1 Overall Effects of Land-Use Systems on C and N Contents

The soil organic matter (SOM) dynamics is influenced by the management, soil preparation, fertilizers, cover crops, and the organic residues generated in the cultivation. In this study, the C fractions accumulation in the soil varied between cropping systems. The conventional tillage favored the greatest loss of total organic C, with 25% reductions in the CT in comparison to the Cerrado. The total organic C values obtained in the current study, which varied from 19 to 26 g kg^{-1}, are similar to other results collected from other long-term experiments carried out in the Cerrado (Figueiredo et al. 2013; Ferreira et al. 2016). The lowest levels of TOC in the system with soil till may be attributed to the increase in decomposition promoted by tillage of the soil and exposition of the SOM protected in the aggregates (Tivet et al. 2013). It is known that tillage induces the processes of decomposition by breakdown and soil exposure (Sheehy et al. 2015), promoting carbon loss (Sá et al. 2014) and increasing GHG emissions (Jantalia et al. 2008; Bayer et al. 2015; Martins et al. 2015) by reducing biological activity. Due to the harmful effects to the soil, there has been an increase in the use of conservation management of soil based on the absence of soil preparation (no-tillage) as it has been considered the best management practice. Corbeels et al. (2016) evaluated the C stocks in areas under no tillage after 20 years and observed that there is a tendency of C saturation in the superficial layer of the soil in this period. The authors also observed that after a period of 11–14 years, the stocks regained higher values than those found in the natural vegetation of the Cerrado.

In the current study, the NT1 system also presented a tendency of C recuperation, with values close to the original levels of the reference area. These results are attributed to the combined effect of the plant residues of the agricultural cultures and the radicle root systems and residues of the forage plants which, when compared to the conventional continuous cropping, exhibits a more positive effect (Piva et al. 2014).

The NT1 system had the highest content of total N (TN). This result may be explained by the greater accumulation of organic residue in the soil of the NT1, promoted by the alternating crops and the use of tropical grass such as Brachiaria, which favors a greater buildup of carbon by the radicle root system. These results indicate the importance of the soil carbon fractionation, where management systems effects may be more easily detectable in tropical Oxisols.

4.2 Effects on Labile Fractions of SOM

The NT2 exhibited the highest contents of LC in the soil, which may be related to the N_2O emissions during the soy cycle, period in which the soil was collected. Sá et al. (2014), evaluating different land-use systems (conventional and no-tillage), also observed that the areas under no-tillage exhibited the highest contents of LC, which varied from 1.99 to 3.52 g kg^{-1} in the superficial layer of the soil (0–25 cm). Our studies have shown that the soil aggregation and the content of total organic C are related (Fig. 8). Therefore, the labile fractions, such as the LC, may increase the formation of aggregates and protect the organic C in the soil (Tivet et al. 2013), favoring the buildup of C in the different SOM pools.

The highest levels of MBC were found in the area under natural vegetation, with a decrease of up to 42% in the area under CT, while systems under no-tillage, compared to the CER, presented reductions which varied between 25 and 32% of MBC. Considering that no-tillage systems do not present soil disturbance, they increase the MBC in comparison to soils which are revolved (Stieven et al. 2014; Meena et al. 2020). Ferreira et al. (2016) observed decreases of up to 40% in MBC concentrations in the conversion of native areas into long-term conventional management systems. The authors attributed this loss of microbial biomass to the pulverization of macroaggregates caused by soil inversion. The assessment of the MBC is a parameter sensitive to changes caused by the land-use systems (Sousa et al. 2015), and it is utilized as a soil quality indicator (Mi et al. 2016). In the NT1, the MBC contents were higher than in the CT, which indicates that the preservation of macroaggregates positively affects the soil microbial population.

Another fraction of SOM which presents high sensibility to soil management is the particulate organic C (POC) (Plaza et al. 2013; Mi et al. 2016), since its buildup is associated with the recent input of plant material of rapid availability to be decomposed by the microorganisms (Duxbury et al. 1989). The current study observed that the levels of POC in the CER varied greatly due to the diversity of the plant material in the sample harvesting areas of the native Cerrado. With respect to the agricultural systems, the soil disturbance affects the TOC buildup and, consequently, the POC content in the soil. Kibet et al. (2016) evaluated the POC in different forms of soil preparation in a long-term experiment (33 years) and concluded that the soil under no-tillage presented the highest POC content, confirming the results of the study, where the highest values of POC were verified in the NT1 and NT2 systems. In these systems, the utilization of the Brachiaria as a cover crop in the interim harvest period propitiates a greater accumulation of POC in the soil, which was also observed in the previous study of Rossi et al. (2012).

In the NT1 and NT2 systems, it should be pointed out that the only difference between them during the crop phase is that in the NT1, there is the occurrence of grazing and excretion on soil by animals in the interim harvest period, all the other practices being very similar. Mi et al. (2016) studied different plant residues applied to the soil and observed that the residues from animal excreta influence the levels of POC in the soil due to its C/N ratio being lower than the residues of plant husks. The intensity of grazing is another factor that also affects the input of C to the soil for TOC and POC, since the greater sources of C are the plant forage residues. Assmann et al. (2014), in a long-term study of integrated crop-livestock system (15 years) in the south of Brazil, proved that intense grazing causes the decrease of 17–33% of the annual addition of C to the soil when compared to areas without grazing. Nicoloso et al. (2008) concluded that the areas managed with grazing in the interim harvest (CT) show a larger addition of C compared to the integrated crop-livestock areas, which have a high grazing frequency.

4.3 Effects on Stable Fractions of SOM

The MOC exhibited lower content in the cropping systems compared to the CER. These results show that the proportions of the stable forms of C are larger where there is no anthropic intervention, resulting in a greater stability of the mineral fraction (Rossi et al. 2012). As its cycling rate is lower, the MOC may be considered a “long-term C storage” (Pinheiro et al. 2015). The buildup of C in the humic fractions depends on high ratios of C/N and lignin/N of the plant residues, which have a slower decomposition speed, favoring the increase of recalcitrant fractions in the soil (Zhongkui et al. 2010).

The humin fraction (HUM-C) presented the highest content of TOC, varying from 26 to 33% among the systems. The results by Silva et al. (2011) report higher values of HUM-C, contributing with 45–75% of the TOC. The native area presented the largest HUM-C content, while the three cropping systems showed no significant differences. However, HUM-C content for the CT system represents around 33% of the TOC, compared to 26% of the other systems, indicating that the CT exhibits an elevated humification (Fig. 5b). These results demonstrate that, although there is less content of TOC in the CT system when compared to the other systems, the largest part of C in this system is humified in the form of HUM-C, seeing that the labile organic residues were rapidly mineralized, promoted by the breakdown of aggregates during soil preparation, forming a readily available deposit of C in the soil (Figueiredo et al. 2013).The smaller content of the humic acid (HA-C) in CER may be a consequence of its plant composition, which is rich in lignin compared to agricultural areas.

4.4 Carbon and Nitrogen in Soil Aggregates

The HA-C/FA-C ratio (Fig. 5a) allows to predict the degree of evolution of humification, as well as to evaluate the capacity of mobility of C in the soil (Kononova 1982). In the current study, the HA-C/FA-C ratio in the cropping areas varied

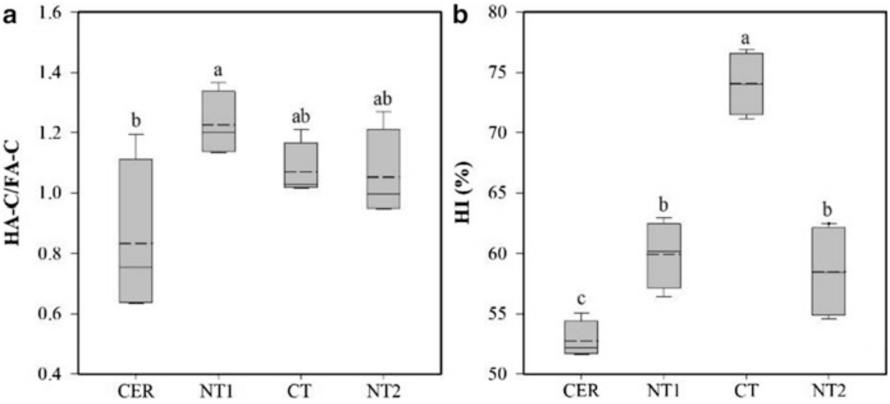

Fig. 5 (**a**) HA-C/FA-C ratio; and (**b**) humification index (HI) in the different land-use systems. Descriptions of treatments are shown in the caption of Fig. 2. Same letters within treatments indicate no difference (Tukey-Kramer; $p < 0.05$)

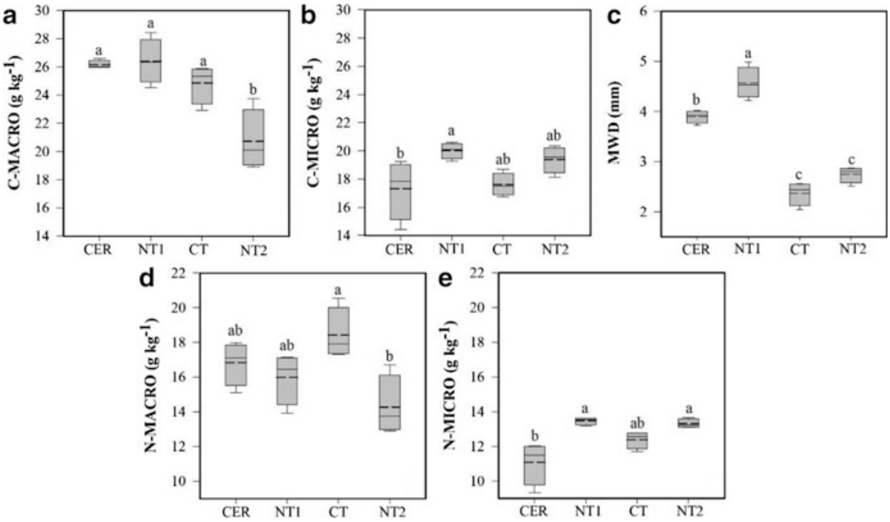

Fig. 6 (**a**) Carbon in macroaggregate soil (C_{MACRO}); (**b**) carbon in microaggregate soil (C_{MICRO}); (**c**) mean weight diameter (MWD) in soil; (**d**) nitrogen in macroaggregate soil (N_{MACRO}); and (**e**) nitrogen in microaggregates (N_{MICRO}) in the different land-use systems. Same letters within treatments indicate no difference (Tukey-Kramer; $p < 0.05$)

between 0.9 and 1.1. This indicates that the soil is in an intermediary process of humification for exhibiting intense mineralization of the plant residues. In the CER, this proportion was low (0.56). These results allow the inference that, over 24 years of experiment, the intense plant residue deposit favors the increase of HA-C

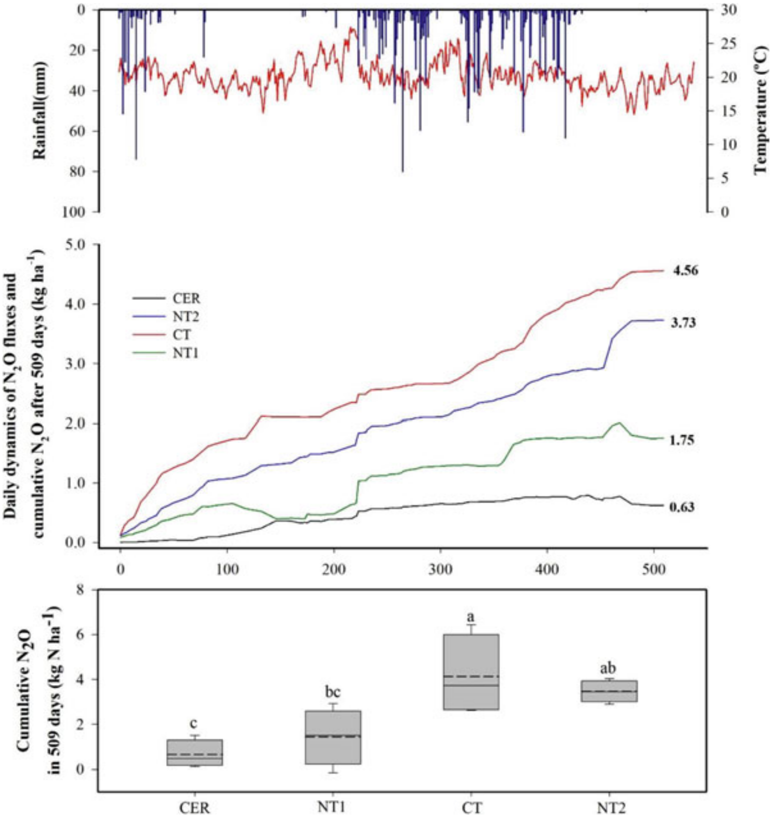

Fig. 7 Rainfall (mm) and average air temperature (°C); daily dynamics of N_2O fluxes and cumulative N_2O after 509 days and boxplot of cumulative N_2O. Same letters within treatments indicate no difference (Tukey-Kramer; $p < 0.05$)

fractions in the soil, due to the low content of lignin in the vegetation cover in the soil compared to the Cerrado area.

In the Cerrado region, there is a great quantity of inert carbon (IC), in charcoal form, derived from wildfires, typical of this region. However, the change of native areas for agricultural production reduced in up to 22% the IC content in continuous crops. In the NT1 system, there was an increase of 15% of this fraction.

The labile fractions of SOM are fundamental for C cycling between compartments and for short-term nutrient cycling, but also contribute to the transitory formation and stability of soil aggregates (Santos et al. 2013). The use of Brachiaria in the agricultural systems is being considered an important factor which favors soil aggregation (Loss et al. 2011; Salton et al. 2014). The results of these study show that the NT1 exhibited larger proportions of aggregates, with a mean weight diameter (MWD) of 4.57 mm. Nowadays, there is a consensus that soils with greater aggregation present a better soil quality than those with similar

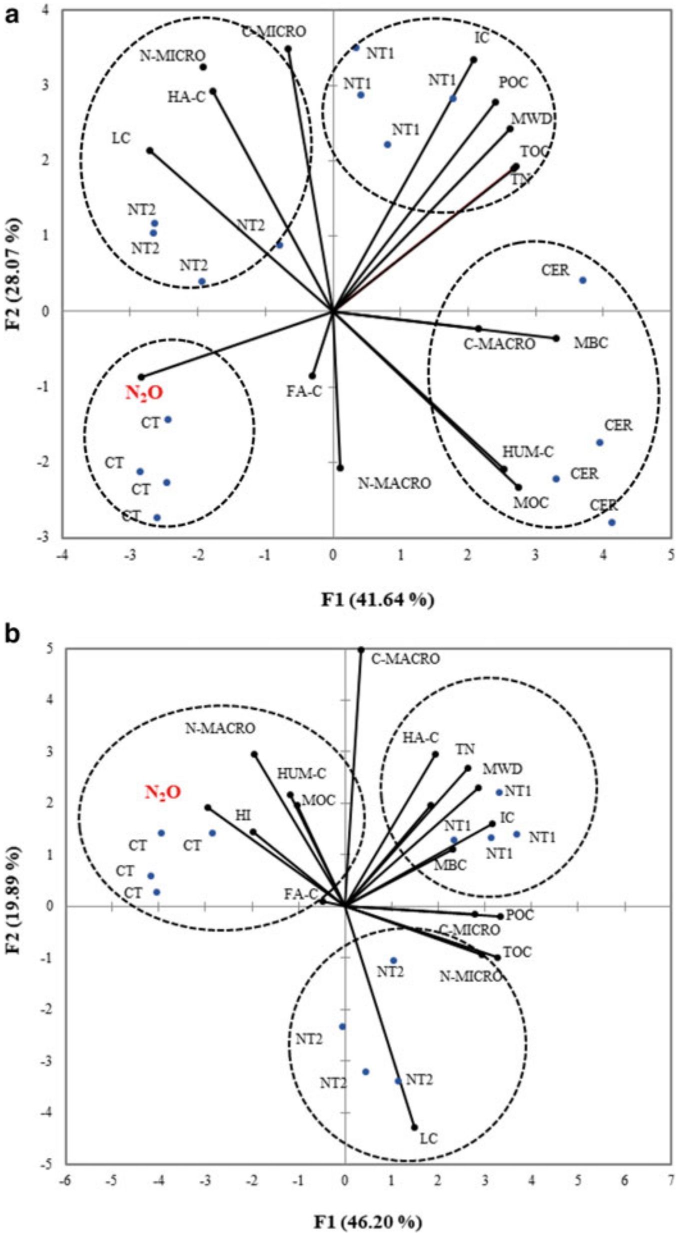

Fig. 8 Principal component analysis (PCA) of the C fractions in the soil and cumulative N_2O emissions after 509 days in the different evaluated systems (**a**) and PCA of C fractions in the soil and cumulative N_2O emissions in the sorghum crop in the agriculture systems (**b**)

characteristics and lesser aggregation, due to the physical protection of carbon provided by greater aggregation (Salton et al. 2014).

Finally, the results of microaggregate C, along with the results of MWD, indicate that the NT1 exhibits greater soil aggregation than the other evaluated systems and a larger C pool in microaggregates than that of the native area. According to Tivet et al. (2013), the greater concentration of organic labile fractions may increase the formation of aggregates, thus protecting the C from the soil physically and chemically impeding its loss to the atmosphere. This demonstrates the potential of the crop-livestock system for the mitigation of GHG, such as N_2O.

4.5 Relationship Between Soil Organic Matter Fractions and N_2O Emissions

The first two principal components of PCA (Fig. 8) explained around 66% of the data variability. PC1 distinguished mainly agricultural systems with a gradient of C and N contents with positive eigenvalues and accumulated N_2O, with negative eigenvalues. PC2 is mainly related to a gradient SOM fractions and aggregation with positive eigenvalues and LC, with negative eigenvalue. The coordinates of the agricultural systems (plots) plotted in the factorial plan shows a grouping (Fig. 8b). Axis 1 clearly separated the NT1 and NT2 from the CT system, which is related mainly to higher N_2O emissions. It is possible to observe that axis 2 distinguished mainly NT2 system from the others with a tendency to high levels of LC. From this result, it is possible to conclude that in the CT system C losses of the most labile fractions occur due to soil plough, which causes higher N_2O emissions. On the other hand, in the conservation systems (NT1 and NT2), these losses are smaller favored by the soil aggregation.

Furthermore, various studies indicate that high quantities of SOM are potentially related to higher N_2O emissions (Kong et al. 2009; Morley and Baggs 2010; Bhattacharyya et al. 2013). In the present study, the NT1 was the agricultural system that emitted the lowest amount of N_2O to the atmosphere and also presented the highest C content in the following fractions: C_{MACRO}, C_{MICRO}, POC, IC, and HA-C. These results show that the lower accumulated emissions of N_2O into the atmosphere may result from a balance between labile and stable fractions of SOM and better protection in aggregates (Sato et al. 2019).

The results obtained from the PCA (Fig. 8b) demonstrate that the N_2O emissions were associated with the CT system, with vector positioning opposite the LC and POC properties. It is possible to conclude that in the CT system, C losses of labile fractions of SOM occur due to soil rotation, which may have resulted in higher N_2O flows. In the conservation systems, these losses are smaller by favoring the aggregation of the soil. The most recalcitrant fractions, such as HUM-C, HA-C, IC, and MOC, in NT1 are possibly related to the low fluxes of N_2O.

The residues of crops with low C/N ratios, such as legumes, also trigger high rates of N_2O emissions (Huang et al. 2004; Millar et al. 2004), since they decompose easily and supply N composts readily available for the soil microorganisms (Miller et al. 2008). Morley and Baggs (2010) showed that the composition of plant residues interferes in N_2O emissions and demonstrate that N_2O emission is favored when the plant residues are more easily converted into simple carbohydrates.

Qiu et al. (2015), in studies with dissolved SOM and GHG emissions in soils in China, verified that the dissolved organic C and the temperature of the soil present a positive relation in N_2O emission from the soil. Therefore, in tropical soil, with a higher clay content, a higher N_2O emission was expected. In view of these results, the present study observed that the NT1, which exhibited the greater content of organic carbon associated with microaggregates (C_{MICRO}), resulted in lower cumulative N_2O emissions. Thus, it was observed that the NT1 is the cropping system with lower emission, proving to be more sustainable and efficient in this aspect, exhibiting a balance that favors mitigation of GHG emissions.

5 Conclusion and Future Prospects

Among the soil attributes that influence the emission of gases, those that are related to the structure and stability of the SOM are determinants of N_2O fluxes. In conservation systems such as NT1, the presence of Brachiaria as a cover crop, in addition to promoting greater total carbon accumulation, also contributes to the formation of soil aggregates, which promote greater protection of SOM and lower N_2O emissions. The results demonstrate that the conventional system reduced all fraction of SOM and decreased the physical protection of SOM and increased the humification index of SOM and, consequently, increased the emission of N_2O to the atmosphere. The NT1 system had the lowest cumulative N_2O emissions. This may be due to the greatest buildup of C in its most stable fractions and occluded in aggregates, confirming the hypothesis that the accumulation of C in the most stable fractions of the soil, unavailable to the microbiota, causes lower emissions of N_2O to the atmosphere. Despite the high SOM content in the crop-livestock system, the predominance of C and N in stable forms and physically protected in aggregates may reduce the emission of N_2O from soils.

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