Soil Organic Carbon Stabilization as Influenced by Clay Minerals

Meti Ranjitha*, Mahalaxmi Shrishail Devarnavadgi, Chaya G B, Adithya Kunal and Veeresh Basavaraj Katti

Ph.D. Scholar, Department of Soil Science and Agricultural Chemistry, UAS, Dharwad-580005, Karnataka, India

Corresponding Author: ranjumetiranju@gmail.com

Introduction

Soil organic carbon (SOC) is one of the largest pools of organic carbon (OC). It ranged from 1462-1584 Pg in the top 100 cm (Batjes, 1996). Organic carbon content in soils is approximately three times more than that of atmospheric or terrestrial pool. The atmospheric concentration of carbon dioxide (CO_2) has increased globally by 40 % from 278 ppm in the preindustrial era to the current value of 410 ppm (GMD, 2017). The CO_2 accounts for about 50 % of the warming effect of all climate-impact gases.

Carbon sequestration refers to capturing atmospheric CO_2 and storing it in a stable form in the soil, thus preventing it from being released back into the atmosphere.

- The amount of carbon sequestered in the soil depends on the balance between the carbon inputs (such as plant residues, organic matter) and carbon outputs (through processes like decomposition, respiration).
- A positive carbon balance means that more carbon is being added to the soil than is being lost, leading to carbon sequestration.
- A negative carbon balance means that more carbon is being lost from the soil than is being added, resulting in carbon degradation.

What is the relative carbon storage efficiency (*i.e.*, carbon stock increase per unit carbon added) for different soils?

The relative carbon storage efficiency, or the increase in carbon stock per unit of carbon added, varies among different soil types based on their physical and chemical properties. Here's a general outline of how different soils perform:

1. **Clay-rich soils (e.g., *Vertisols*-Smectitic soils)**
   - **High storage efficiency**: These soils have a larger surface area and higher cation exchange capacity (CEC), which allows them to adsorb and protect more organic carbon. The clay particles can physically and chemically protect carbon from decomposition.
     - **Smectitic soils** have particularly high efficiency due to their ability to form strong organo-mineral associations.

2. **Sandy soils**
   - **Low storage efficiency**: Sandy soils have lower surface area and limited ability to protect organic carbon. Carbon added to sandy soils is more prone to decomposition due to less physical protection.

3. ***Allophanic* and *Andisols***
   - **Moderate to high efficiency**: These soils, rich in amorphous minerals like allophane, are highly effective at stabilizing carbon due to their high reactivity and large surface area. They can form strong bonds with organic matter, helping retain carbon.

4. ***Alfisols* and *Oxisols***
   - **Moderate efficiency**: These soils have lower carbon storage capacity compared to clay-rich soils. Oxisols, with high iron and aluminum oxides, can adsorb carbon, but they may also have lower overall organic matter due to intense weathering.

5. **Peaty soils (Histosols)**
   - **High inherent carbon stocks**, but their ability to increase storage with added carbon is lower as these soils are already carbon-rich.

Whether SOC stocks increase infinitely with greater carbon input or is there an upper limit to the capacity for soils to store carbon?

SOC stocks do not increase in infinitely with greater carbon input, there is an inneed upper limit to the capacity for soils to store carbon. Soils have a saturation point beyond which they cannot effectively store additional carbon.

Carbon saturation: Soil carbon saturation is then defined as a soil's unique limit to carbon stabilization as a function of C input levels based on the cumulative behavior of four carbon pools (*i.e.*,

chemically, physically, biochemically protected and non-protected pools).
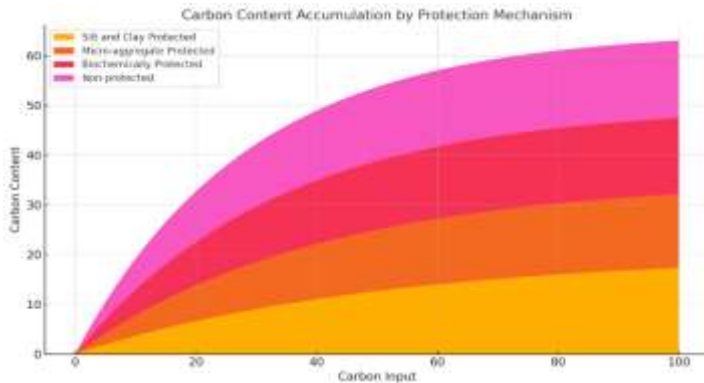
Fig 1. The graph illustrates how different types of soil organic carbon (SOC) behave as carbon is added to the soil

Saturation Point: The soil eventually reaches a point where it can't store any more carbon. This is the "saturation level," and it depends on factors like soil type and management practices.

Types of Carbon Protection

- **Non-protected Carbon**: This is the most easily decomposable carbon in the soil. It increases quickly with carbon input but can also break down quickly.

- **Biochemically Protected Carbon**: This carbon is protected by chemical compounds, making it harder for microbes to break down. It increases at a slower rate compared to non-protected carbon.

- **Microaggregate-Protected Carbon**: Here, carbon is physically protected within small soil structures called microaggregates. This offers better protection than the first two types.

- **Silt and Clay-Protected Carbon**: Carbon bound to fine particles like silt and clay is the most stable. Even with more carbon inputs, this fraction grows very slowly because it's already well-protected from decomposition.

I.1. Soil Organic Carbon Stabilization

Soil organic carbon stabilization can be termed as any action which slows down the decomposition of soil organic matter by reducing the mineralization rate.

I.2. Mechanism of soil organic carbon stabilization

There are three main mechanisms of C stabilization: (a) physical, (b) chemical, and (c) biological (or biochemical). Various processes and reactions underpinning these mechanisms are shown in Fig. 2 and explained in the following sections.
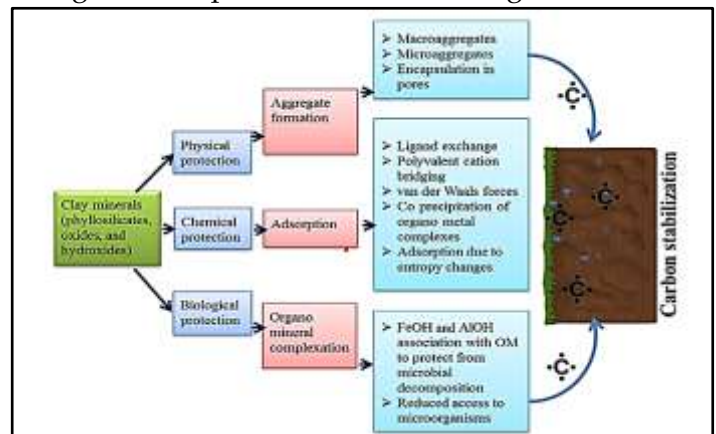
Fig 2. Mechanisms of C stabilization in soils by clay minerals

a) Physical Protection

Physical stabilization of organic matter (OM) happens when soil structure creates physical barriers that protect OM from decomposers. The separation of soil into compartments limits access to oxygen, water, enzymes, and microbes, reducing decomposition. Microbes tend to concentrate on the outer surfaces of soil aggregates, while OM is stored inside. Soil aggregation helps accumulate OM, and breaking these aggregates, such as through cultivation, releases carbon and speeds up decomposition. Overall, maintaining intact soil aggregates is crucial for protecting OM from breakdown.

b) Chemical Protection

Chemical protection of soil organic carbon (SOC) occurs through several mechanisms that involve the adsorption between organic matter and soil minerals:

- Ligand Exchange: Organic molecules containing functional groups (like carboxyl or phenolic groups) form direct chemical bonds with mineral surfaces, especially oxides of Fe and Al. This creates strong, stable associations between the organic carbon and minerals, reducing decomposition.

- Cation Bridge: Divalent or trivalent cations (e.g., Ca^{2+}, Fe^{3+}, Al^{3+}) act as a bridge between negatively charged organic matter and negatively charged clay or mineral surfaces, effectively binding the organic matter to the mineral and enhancing stabilization.

- Van der Waals Forces: These weak forces occur when organic matter is physically adsorbed onto mineral surfaces through non-covalent, attractive forces, providing some degree of protection. Though weaker than ligand exchange or cation bridges, van der Waals forces still contribute to carbon stabilization.

- Adsorption due to Entropy: Organic molecules may be adsorbed onto mineral surfaces due to entropy-driven processes, where the disordered state of the system increases by reducing free molecules in the solution. This can happen even without strong chemical bonds, leading to the retention of organic carbon on mineral surfaces.

Together, these mechanisms reduce the accessibility of SOC to decomposers and enzymes, thus enhancing its stability in the soil.

c) Biological Protection

Biological protection of soil organic matter (OM) occurs through organo-mineral complexation, where organic matter associates with iron (FeOH) and aluminum (AlOH) hydroxides. This complexation forms stable structures that effectively shield organic carbon from microbial decomposition. By binding with these metal hydroxides, the access of microorganisms to the organic matter is significantly reduced, limiting their ability to break it down. This protective mechanism enhances the stability of soil organic carbon (SOC) by creating physical and chemical barriers, thereby promoting long-term carbon storage in the soil. Ultimately, the association with Fe and Al hydroxides plays a crucial role in maintaining soil health and fertility by preserving organic matter.

I.3. Soil clay minerals and their properties (Table 1.)

Clay mineral name	Type	Specific surface area (m² g⁻¹)	Cation Exchange capacity (cmol (p⁺)kg⁻¹)
Kaolinite	1:1 silicate (non-expanding)	5-30	3-15
Montmorillonite	2:1 silicate (expanding)	700–800	80–120
Vermiculite	2:1 silicate (limit expanding)	650–700	100–150
Illite	2:1 silicate (non expanding)	70-100	20-40
Allophane	Non-cystalline silicate	700-1500	pH variable (20-50)
Gibbsite	Al oxide (non-silicate)	80-200	pH variable
Goethite	Fe oxide (non-silicate)	14-77	pH variable
Hematite	Fe oxide (non-silicate)	35-45	pH variable
Ferrihydrite	Non-cystalline silicate	200-500	pH variable

Silicate clay minerals:

1:1 clay mineral like kaolinite consists of one tetrahedral and one octahedral sheet, tightly bound by ionic and hydrogen bonds, leaving minimal interlayer space. This restricts water and cation entry, resulting in low cation exchange capacity (CEC) and limited charge development. Due to their larger particle size, strong interlayer bonding, and lack of isomorphous substitution, 1:1 clay has lower specific surface area and exhibit minimal shrink-swell behaviour and plasticity.

Montmorillonite (2:1 type) has high surface charges due to isomorphous substitution in both octa- and tetra-hedral positions. The Cation exchange capacity (CEC) of Montmorillonite is very high. Montmorillonite has very high specific surface area. High specific surface area of montmorillonite is attributed to higher extent of internal surface area.

Vermiculite is a 2:1 clay mineral, meaning it has two tetrahedral sheets surrounding one octahedral sheet. It has a moderate expansion capability due to water and cations entering the interlayer space. Vermiculite has a high specific surface area (SSA), generally ranging from 650–700 m²/g, and a high cation exchange capacity (CEC), typically between 100–150 meq/100g. This high CEC is due to significant isomorphous substitution, where magnesium and iron replace aluminum in the octahedral sheet, resulting in a permanent negative charge is a non-expanding 2:1 clay mineral with a structure similar to montmorillonite but has potassium ions that limit its swelling ability. It has a

moderate CEC (20–40 meq/100g) and a relatively low specific surface area compared to smectites.

Non silicate minerals

Allophane is an amorphous (non-crystalline) aluminosilicate with high reactivity. Due to its amorphous nature, it has a large specific surface area and high CEC (20–50 meq/100g).

Ferrihydrite is an amorphous iron oxide that has a high specific surface area and is highly reactive. It plays a crucial role in phosphorus retention in soils, although it has a very low CEC.

Iron oxide minerals, such as goethite (FeOOH) and hematite (Fe_2O_3), play key roles in soil formation and nutrient cycling. They have low cation exchange capacity (CEC), but their high specific surface area allows them to adsorb and retain phosphorus and other anions. These minerals are stable, contribute to soil structure, and influence soil aeration and drainage, particularly in tropical and highly weathered soils.

I.4. Influence of clay minerals on carbon stabilization

Phyllosilicate Minerals

1. Inactivation of Enzymes

Phyllosilicate minerals, such as clay minerals, have a strong adsorption capacity for organic molecules and enzymes. When enzymes involved in the biodegradation of organic matter (OM) adsorb onto clay surfaces, their active sites may become obstructed or altered, leading to reduced enzymatic activity. This process effectively inactivates the enzymes, which are crucial for breaking down complex organic substrates into simpler compounds.

2. Reduced Availability of Substrate Organic Molecules

When organic molecules adsorb onto clay minerals, they become less available to microorganisms and enzymes. This reduced accessibility can limit the breakdown of organic materials, leading to slower decomposition rates. The adsorption process effectively shields organic substrates from microbial attack, resulting in an accumulation of organic matter in the soil, which can influence soil fertility and carbon sequestration.

3. Decreased Microbial Activity

The presence of phyllosilicate minerals can inhibit microbial activity due to several factors, including limited availability of nutrients and physical protection of organic matter. Reduced microbial activity can slow down the overall process of organic matter decomposition, which is critical for nutrient cycling in soils. Consequently, this can affect soil health and plant growth.

Other Secondary Minerals

- Protection of Organic Matter through Complexation: Secondary minerals, such as iron (Fe) and aluminium (Al) oxides, play a significant role in stabilizing organic matter through complexation. These minerals can form strong bonds with organic compounds, creating stable associations that protect the organic matter from microbial degradation. The formation of these complexes helps to preserve soil organic carbon, enhancing its long-term stability and reducing the risk of carbon loss through mineralization.

- The presence of free iron and aluminium can lead to reduced bacterial activity, further influencing the degradation of organic matter.

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