

# Inorganic Carbon Sequestration Alters Global Carbon Cycle and Ecosystem Services in Soil

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**Abstract:** Carbon (C) is one of the most important elements found on earth and is directly linked with ecosystem services. Organic C sequestration is a promising strategy to reduce carbon dioxide (CO<sub>2</sub>) concentration in the atmosphere. However, the benefits of organic C sequestration can be counter balanced by the release of releasing CO<sub>2</sub> from soil inorganic carbon (SIC) stocks, which are dominant C stocks in 54% of soils worldwide and amounts to about >2300 Gt in the top 2 meter. Often, this CO<sub>2</sub> source is neglected because of the general belief that SIC is an inert C pool. However, SIC gets lost to the atmosphere progressively, because of anthropogenic acidification and other man made processes. Approximately 1.13 Gt C will be lost irrecoverably by 2050 due to fertilization-induced acidity. Acidification induced SIC losses results in loss of basic cations from the soil, causing Ca<sup>2+</sup> and Mg<sup>2+</sup> deficiencies, responsible for severe yield reduction. In Mollisols is both significant sources of CO<sub>2</sub> from organic matter decomposition and a sink of carbon through pedogenic carbonate formation. Ecosystem services provided by soil, based on natural SIC, is specifically linked for achieve food security and sustainable agriculture; if its replacement cost is determined based on an average price of limestone, the estimate for upper two meters of soil was found between 2.16 to 8.97 trillion U.S. dollars.

## INTRODUCTION

Carbon (C) is one of the most important elements found on earth. The carbon cycle supports all life by transferring carbon between living things and the environment. Across the globe, carbon is stored in different places and in different forms. The amount of carbon stored in a particular system is called a “stock” or a “pool”. The removal of carbon from the atmosphere to relatively stable storage in the terrestrial system is known as soil carbon sequestration (Lal and Bruce, 1999). In soil, carbon stored in organic and inorganic form, although their percentage distribution varied from types of soil, climatic conditions, plantation patterns, physiography of the system etc. Soil inorganic carbon (SIC) is generally disregarded as a C stock compared to soil organic carbon (SOC), because it is assumed to be much more stable and less sensitive to agricultural activities

within the human life timescale. The global soil inorganic carbon pool is primarily located in arid and semi-arid regions, accounting for 90% of the total soil C stock. In arid and semiarid climate, calcareous soils account for approximately 50% of the earth’s surface and approximately 9 billion hectares of arable land worldwide. However recent study revealed agricultural practices cause a rapid drop in the SIC pool. Soil acidification, water flow and recharge, and land-use changes can decrease SIC stocks within a few decades. Even in deep layers SIC stocks are vulnerable to loss through agricultural practices and the losses from this massive pool and their contribution to global climate change are generally neglected which is most important for ecosystem services. Ecosystem service refers to the attributes and processes through which natural and managed ecosystems sustain ecosystem functions, and

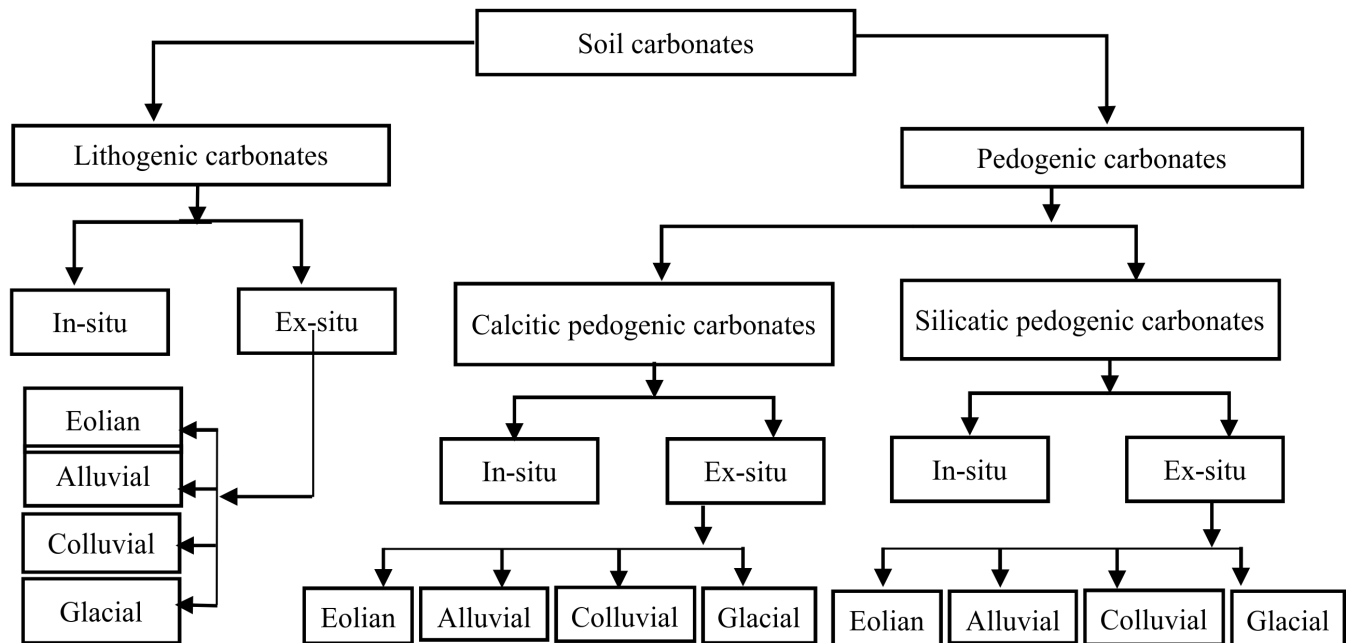


Figure 1: Types of soil inorganic carbon.

create environments so that planetary life can thrive and flourish (Power, 2010). The soil ecosystem services include: carbon sequestration, provide food, fiber and fuel, nutrient cycling, habitat for microorganism, purification of contaminants, source of pharmaceuticals and genetic resources, flood regulation, provide construction material, foundation for infrastructure and cultural heritage. Hence, this review article mainly deals with why inorganic carbon sequestration as much as important as organic carbon sequestration as the it contributes more stable pools of carbon than organic fractions, lots of functions of soil ecosystem services are dependent upon the soil inorganic carbon.

### SOIL INORGANIC CARBON STOCKS AND TYPES

The global contribution of inorganic carbon to the atmospheric carbon dioxide is from two sources i.e. acidification of carbonate-containing soils and those receiving lime which is more than one third of the irrecoverable C from all organic sources together. The contribution of SIC in atmospheric CO<sub>2</sub> over the last 50 years and estimated (0.41 Gt C) the CO<sub>2</sub> release from SIC till 2050 if fertilization and anthropogenic soil acidification remain stable (1.13 Gt C) (Zamanian et al., 2021). By assuming

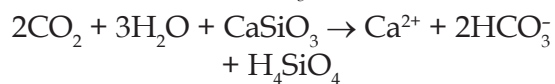
the recent average liming amount of one-ton lime per hectare, about 8.2 Gt C will be emitted as CO<sub>2</sub> from the acid soils until 2050.

Soil carbonates also known as soil inorganic carbon are classified into lithogenic carbonate and pedogenic carbonates (Figure 1), lithogenic carbonate refers to detrital particles derived from carbonate rock (mainly limestone) that formed in aquatic environments whereas Pedogenic carbonate refers to carbonate formed in soils authigenically, which is common in arid, semiarid, and some sub-humid climates that is further divided based on source of calcium, if it is from pre-existing limestone it is known as calcitic pedogenic carbonate and silicatic if calcium is derived from silicates minerals. This classification is further divided into *ex situ* or *in situ*, *in situ* indicates residual limestone fragments and *ex situ* indicates transport from other locations and is divided into eolian, alluvial, colluvial, or glacial.

### INORGANIC CARBON SEQUESTRATION

Inorganic carbon sequestration generally occurs in soil through unidirectional and equilibrium approach. Weathering of Ca silicates and Mg silicates is the primary factor governing the long-term concentration of CO<sub>2</sub> in earth's

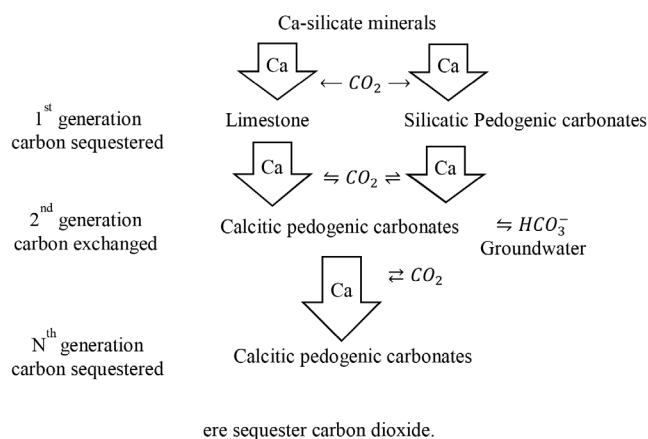
atmosphere because the released  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are precipitated as marine carbonates, thus consuming  $\text{CO}_2$  released by mantle degassing. It also represents short-term soil profile weathering and accumulation of pedogenic carbonates in “non-flushing” soils in arid and semiarid regions. This type of reaction mainly dominates in igneous terrane. This method of sequestration tracks carbon sequestration in soil as well as groundwater. In soil, two moles of  $\text{CO}_2$  react with one mole of Ca silicate resulting in one mole of carbon sequestered as pedogenic  $\text{CaCO}_3$  and one mole of carbon released as  $\text{CO}_2$ . In groundwater, one mole of  $\text{Ca}^{2+}$  and two moles of  $\text{HCO}_3^-$  can be stored. However, this is temporary storage that lasts until  $\text{HCO}_3^-$  combines with  $\text{Ca}^{2+}$  and precipitates as  $\text{CaCO}_3$ .



In soils of dry climates, limestone is dissolved by carbonic acid and produces  $\text{Ca}^{2+}$  and  $2\text{HCO}_3^-$ , which re-precipitate as pedogenic  $\text{CaCO}_3$ . This re-precipitated pedogenic  $\text{CaCO}_3$ , however, does not sequester atmospheric carbon because the source of Ca is from pre-existing  $\text{CaCO}_3$  and the  $\text{CO}_2$  that is consumed in the reaction to form carbonic acid is released upon the reprecipitation of  $\text{CaCO}_3$ . In soils of humid climates, limestone also is dissolved by carbonic acid, but instead of remaining in the soil profile,  $\text{Ca}^{2+}$  and  $2\text{HCO}_3^-$  are transported to groundwater which serves as a temporary pool for carbon sequestration. The dissolution of limestone is estimated to sequester 12 Tg of carbon per year. Eventually,  $\text{Ca}^{2+}$  and  $2\text{HCO}_3^-$  in groundwater are transported to streams and the oceans where they are biologically precipitated as limestone ( $\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightleftharpoons \text{Ca} + \text{CO}_2$ )

Chemical weathering of Ca silicates via the Ebelmen-Urey reaction consumes atmospheric  $\text{CO}_2$  and sequesters carbon in limestone at the continental scale and in silicatic pedogenic carbonate at the soil profile scale. These forms of  $\text{CaCO}_3$  are designated first generation (Figure 2). The subsequent dissolution of limestone and silicatic pedogenic carbonate via the carbonate dissolution-precipitation reaction consumes

one mole of atmospheric  $\text{CO}_2$  during the dissolution phase, but re-emits it during the precipitation phase. Thus, carbon is exchanged, but not sequestered. Calcitic pedogenic carbonate is designated second generation. Now the successive dissolution-precipitation cycles occur via the same reaction and these are designated N<sup>th</sup> generations and no carbon is sequestered, only exchanged. For the purposes of carbon sequestration by soil carbonate, Ca can be used only once – when it is released from silicates. In groundwater, however, carbon can be sequestered as  $\text{HCO}_3^-$  regardless of whether Ca is from silicates or carbonates.



**Figure 2. carbonate generations where sequester carbon dioxide**

## EFFECT OF LOSS OF SOIL INORGANIC CARBON

Soil inorganic C loss resulting from acidification and higher water availability leads to the loss of base cations from the soil, causing calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) deficiencies. Acidification-induced  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  deficiencies in soil are increasing worldwide and causing severe yield reduction or crop failure in many countries. The N fixation capacity of systems under natural and anthropogenic acidification legumes is significantly reduced in carbonate-free soils at pH values below 6 (Zamanian *et al.*, 2018). Moreover, soil acidity limits rhizobium survival and deteriorates the symbiotic relationship between rhizobia and legumes, and inhibits nitrogenase activity. Carbonate-free soils exhibit increased bioavailability and mobility of heavy metals that are toxic to plants. Researchers

also reported that the grains of winter wheat grown in carbonate-free soils accumulates twice Cd and thrice Ni than wheat grains harvested from carbonate-containing soils. Abundance of  $Al^{3+}$  and deficiency of  $Ca^{2+}$ ,  $Mg^{2+}$  considerably offset the nutritional balance, which severely reduces the yield, quality, and root growth of crops. Therefore, carbonate losses from soils not only decrease the soil pH but also influences many processes that consequently affect food production, food quality, and soil health (Raza et al., 2021). Loss of inorganic carbon from carbonates dominated soil (pH 6.5-8.5) affects the soil-plant system differently than and without carbonates soil (pH 4.0-6.5)(Table 1).

**Table 1: Changes in properties of soil with carbonates and without carbonates.**

S. No.	Soil Physical and Chemical properties	Soil biological properties and plant growth
Soil without carbonates		
	Bulk density increases	Earthworm population decreases
	Poor soil structure and aggregate stability	Fungi : bacteria ratio increases
	Weaker soil buffering systems	Microbial biomass diversity decreases
	Chlorite changes to vermiculite and finally collapse to vermiculite	Minerals weathering increases
	$Ca^{2+}$ , $Mg^{2+}$ , $K^+$ availability decreases	Soil borne diseases increases
	Metal oxides replaces $Ca^{2+}$ as organic matter stabilizers	Stunted root growth
	Heavy metals availability increases, $Al^{3+}$ , $Mn^{2+}$ and Cd toxicity increases	Root penetration decreases
Soil with carbonates		
	Bulk density decreases	Deep root penetration
	Aeration and water permeability increases	Resistance against pathogens and abiotic stresses increases
	Organic matter stability increases	Microbial biomass diversity decreases
	Buffering capacity increases, Nutrient availability increases	Balanced fungi : bacteria ratio
	P, Fe and Zn availability decreases, heavy metal toxicity decreases, soil erosion decreases	Microbial abundance and activity increases
	Basic cation and $HCO_3^-$ leaching increases	Soil borne diseases decreases

## SOIL ECOSYSTEM SERVICES

The soil ecosystem services include: carbon sequestration, provide food, fiber and fuel, nutrient cycling, habitat for microorganism, purification of contaminants, source of pharmaceuticals and genetic resources, flood regulation, provide construction material, foundation for infrastructure and cultural heritage. Inclusion of SIC into the list of key soil properties linked to ecosystem services through soil functions for the well-being of humans is important for achieving the Sustainable Development Goals (SDGs) to sustain global human societies. Soil inorganic carbon is a component of total carbon (TC), which is composed of both SOC and SIC. Soil inorganic carbon belongs to soil chemical properties, and its soil functions include cycling of elements (e.g.,  $Ca^{2+}$ ), elemental transformation, buffering (e.g., soil pH) and leaching (e.g., bicarbonates). The significance of SIC in agriculture (especially as a liming equivalent) is well documented and the following examples are specifically linked to the selected: End hunger, achieve food security and improve nutrition and promote sustainable agriculture; Naturally present SIC includes numerous beneficial liming impacts on soils such as increased nutrients and biota, improved soil structure, which promotes sustainable agriculture and food security. Calcium in SIC contributes to increased yield of grain and biomass (often through impacts on nutrient cycling) which has direct implications for food security. Grasslands biomass and nutrients increase which improves livestock growth and therefore food production (as shown through liming addition studies). Ensure healthy lives and promote well-being for all at all ages; Soil is a supplier of macro- and micronutrients necessary for human health. Soil inorganic carbon is a source of macronutrients (e.g., calcium and magnesium) which are essential for human health. Ensure availability and sustainable management of water and sanitation for all; Soil inorganic carbon can likely counteract acid deposition thereby protecting water quality and may reduce  $NO_3^-$  leaching. Protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification and halt and

reverse land degradation and biodiversity loss. Highest species richness often is highest in pH-neutral soils and falls significantly below a pH of 5. Soil calcium availability from SIC-rich soils may positively impact higher trophic levels, with initial evidence that some birds may benefit as shown through liming studies.

## EFFECTS OF SOIL INORGANIC CARBON ON CARBON CYCLE AND ECOSYSTEM SERVICES

The positive correlation between exchangeable calcium and SOC explained by their simple co-occurrence as an increase in SOC concentration generally increases the cation exchange capacity (CEC) of a soil (Rowley et al., 2018). Calcium is a plant macronutrient and there is evidence that Ca also has a localised positive effect on net primary productivity (NPP) and soil organic matter inputs through above-ground and below-ground biomass. This localised effect on NPP has been shown to positively influence the accumulation of SOC in limed soils. At molecular level calcium is involved in formation of inner sphere as well as outer sphere complex that further stabilizes soil organic carbon in soil. It is a widely established fact that poorly crystalline Fe forms can stabilise SOC. The presence of  $\text{CaCO}_3$  also indirectly participate in the stabilisation of poorly crystalline Fe forms, Ca-Fe interactions, where sorption of Ca by Fe oxides can prevent their further crystallisation, which in turn, may exert a positive feedback on the retention of SOC by involving ternary Fe-Ca-SOC complexes.

Soil organic carbon approximately twice as high at the  $\text{CaCO}_3$ -bearing site compared to the  $\text{CaCO}_3$ -free site (Rowley et al., 2020). This accumulation could involve the higher primary productivity of grasses at the  $\text{CaCO}_3$ -bearing site. Increased root turnover or exudation at the  $\text{CaCO}_3$ -bearing site could explain part of the differences in SOC, but this effect should be relatively small due to the similarities between vegetation structure at the sites. Secondly, difference in the efficiency of SOC stabilisation that drove the relative accumulation of SOC observed at the  $\text{CaCO}_3$ -bearing site. Total nitrogen followed an almost identical pattern and higher at the  $\text{CaCO}_3$ -bearing site ( $0.6 \pm 0.0\%$ )

than at the  $\text{CaCO}_3$ -free ( $0.3 \pm 0.0\%$ ) (Rowley et al., 2020). The contributions of SIC –  $\text{CO}_2$  to total  $\text{CO}_2$  emissions is between 15 and 30% in topsoil layers and between 50 and 70% in subsoil layers. In topsoil layers, most of the total emitted  $\text{CO}_2$  originated from SOC, whereas in deep soil layers it mainly originated from SIC (Cardinael et al., 2020). The decrease in soil organic carbon stocks as a result of cultivation. The decrease in soil organic carbon stocks in 0–1 m depth varied by soil type and associated landscape position and decreased from 3 to 35 t C ha<sup>-1</sup> at different sites (Mikhailova et al. 2009). In the Russian Chernozem, the soil organic carbon stock decreased as a result of cultivation by 66 t C ha<sup>-1</sup> in the 0–1 m depth, and by 113 t C ha<sup>-1</sup> in the 0– to 2-m depth.

Value of soil inorganic carbon for ecosystem services through liming replacement costs

Soil inorganic carbon naturally occurring in the soil provides a substantial monetary value. Soil potential method to assess the value of SIC is by determining its replacement cost based on the price of commercial limestone that would be required to amend soil. Groshans *et al.* (2018) calculated replacement cost value of SIC based on an average price of limestone. It was found that total replacement cost value of SIC in the upper two meters of soil is between 2.16 to 8.97 trillion U.S. dollars. The replacement values of SIC varies by soil order, depth and region. The significance of SIC in agriculture especially as a liming equivalent is not well documented and it is specifically linked to the sustainable developments goals which includes end hunger, achieve food security, improve nutrition and promote sustainable agriculture.

## CONCLUSIONS

Soil inorganic carbon contributes significantly to the total carbon stocks especially in calcareous soil and that can be ranged from 20 to 60% depending on soil depth. Soil inorganic carbon originated  $\text{CO}_2$  emissions owing to acidity neutralization in calcareous and limed soils are very high, which can offset the benefits of C sequestration as SOC. Mollisols appear to be both a significant source of  $\text{CO}_2$  from organic matter decomposition and a sink of carbon through

pedogenic carbonate formation. Soil inorganic carbon losses from soil deteriorate soil health, decrease plant productivity, increase heavy metal availability, and consequently threaten global food security and human health. Economic valuations of ecosystem services carried out by soil inorganic carbon must be evaluated. Besides that lots of comprehended research is required for better understating of soil inorganic carbon and prevent their losses.

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