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Review

Soil Inorganic Carbon as a Potential Sink in Carbon Storage in Dryland Soils—A Review

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Abstract: Soil organic carbon (SOC) pool has been extensively studied in the carbon (C) cycling of terrestrial ecosystems. In dryland regions, however, soil inorganic carbon (SIC) has received increasing attention due to the high accumulation of SIC in arid soils contributed by its high temperature, low soil moisture, less vegetation, high salinity, and poor microbial activities. SIC storage in dryland soils is a complex process comprising multiple interactions of several factors such as climate, land use types, farm management practices, irrigation, inherent soil properties, soil biotic factors, etc. In addition, soil C studies in deeper layers of drylands have opened-up several study aspects on SIC storage. This review explains the mechanisms of SIC formation in dryland soils and critically discusses the SIC content in arid and semi-arid soils as compared to SOC. It also addresses the complex relationship between SIC and SOC in dryland soils. This review gives an overview of how climate change and anthropogenic management of soil might affect the SIC storage in dryland soils. Dryland soils could be an efficient sink in C sequestration through the formation of secondary carbonates. The review highlights the importance of an in-depth understanding of the C cycle in arid soils and emphasizes that SIC dynamics must be looked into broader perspective vis-à-vis C sequestration and climate change mitigation.

Keywords: arid; carbonate; carbon sequestration; climate change; pedogenic carbonate

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Citation: Naorem, A.; Jayaraman, S.; Dalal, R.C.; Patra, A.; Rao, C.S.; Lal, R. Soil Inorganic Carbon as a Potential Sink in Carbon Storage in Dryland Soils—A Review. *Agriculture* **2022**, *12*, 1256. https://doi.org/10.3390/agriculture12081256

Academic Editor: Luca Vitale

Received: 21 July 2022
Accepted: 16 August 2022
Published: 18 August 2022

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1. Introduction

The dynamics of total soil carbon (C) are influenced by rising temperatures, high CO_2 concentrations in the atmosphere [1], land use changes, and soil management methods [2]. In this regard, C sequestration is being extensively researched to mitigate the negative impacts of rising atmospheric CO_2 levels. Carbon sequestration entails trapping CO_2 at large and stationary sources, transporting CO_2 from the source to a sink, and storing CO_2 in a large sink such as a soil system [3]. The soil system is a clear example of a significant sink as well as a source of atmospheric CO_2, making it one of the primary regulators of C capture and storage and plays a significant role in the C cycle [4]. As a result, soil C is one of the largest C pools in the terrestrial ecosystem, even greater than the combined C pools of the biosphere and atmosphere [5]. The major C pools in the Earth system can be divided into five groups. Figure 1 depicts the five global C pools in the Earth: lithosphere (mainly fossil fuel, mined and combusted at 8 Pg C per year), oceanic (increasing at 2.3 Pg C per year), soil C comprising both SOC and SIC, atmospheric (increasing at 4 Pg C per year) and the biotic C pool comprising both detritus material/necromass and live biomass). The terrestrial pools (both the soil and biotic C pools) is 3.2 times larger than the atmospheric pool. However, these terrestrial pools are frequently altered by anthropogenic activities.

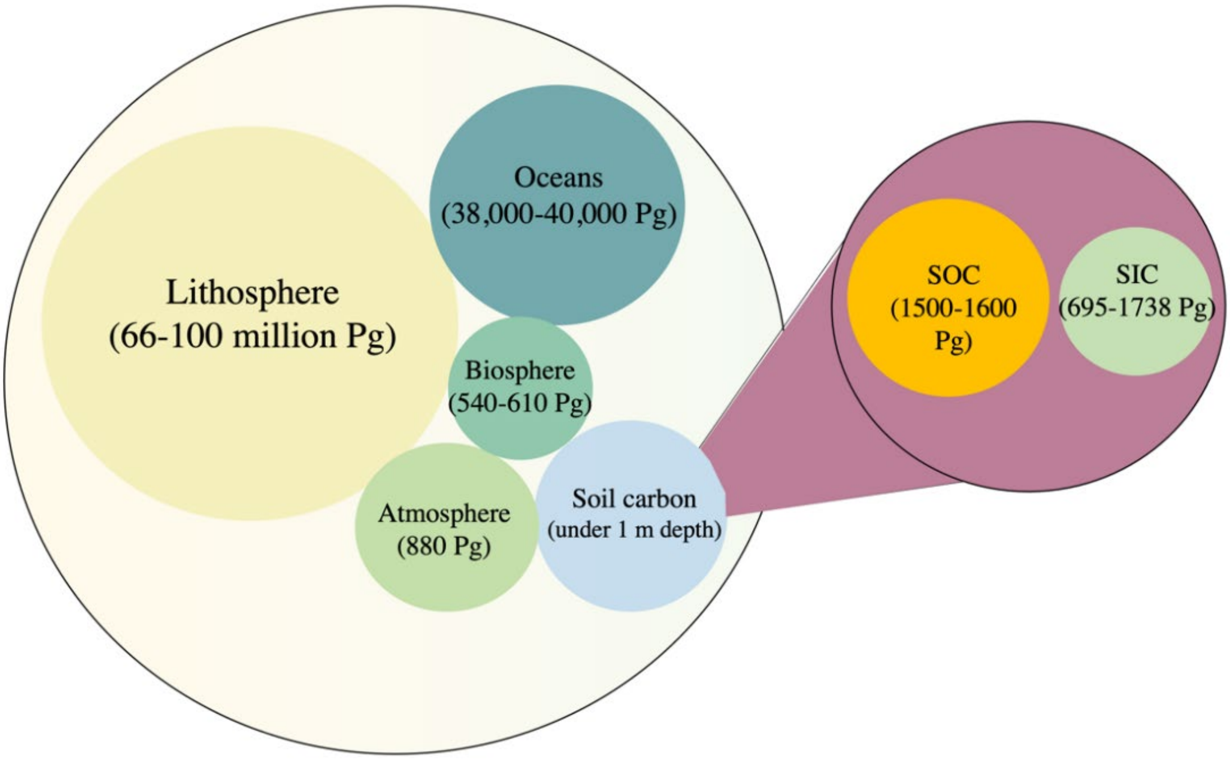

Figure 1. Major pools of carbon in the Earth System (Pg = Petagrams = 10^{15} g) [5–10].

Figure 2 depicts the distribution of total C stock in dryland soils from various regions throughout the world [11]. C storage estimates in these regions are sensitive to changes in land use types. However, this global overview shows that dryland C stock accounts for more than one-third of the global C stock. It is important to note that a large percentage of C is concentrated in dryland ecosystems. Regions such as Africa and the Middle East have a high proportion of C in drylands. However, in other regions such as South East Asia, where moist forests contain a higher amount of C, dryland C storage is still significant. Soil organic carbon (SOC) and soil inorganic carbon (SIC) storage under 1 m soil depth are estimated to be 1200–1600 and 695–940 Pg, respectively, on a global scale [6,12–14]. Even though worldwide SIC storage is less than SOC, the majority of SIC is stored in arid and semi-arid regions [15]. SIC is an unsung player in the global C cycle and needs in-depth and detailed studies and understanding. Thus, dryland soils could be an efficient sink in C sequestration via carbonate formation [16]. Given the large demographic area covered by arid and semi-arid ecosystems, it is hypothesized that these soils can absorb up to 5.2 Pg of C per year [17]. Understanding the factors that influence SIC change/variation is critical for comprehending the potential implications of both climatic and anthropogenic effects on SIC storage in dryland soils. The purpose of this review is to better understand the mechanisms of SIC formation, particularly in dryland soils, which receive less attention and relevance globally. Furthermore, the integrated studies conducted in dryland areas shed light on the dynamic nature of carbonates and the capacity of arid soils in C sequestration and long-term crop productivity. This review paper also emphasizes the importance of a thorough understanding of the C cycle in arid soils and SIC dynamics in relation to C sequestration, as well as the need to mitigate the effects of climate change.

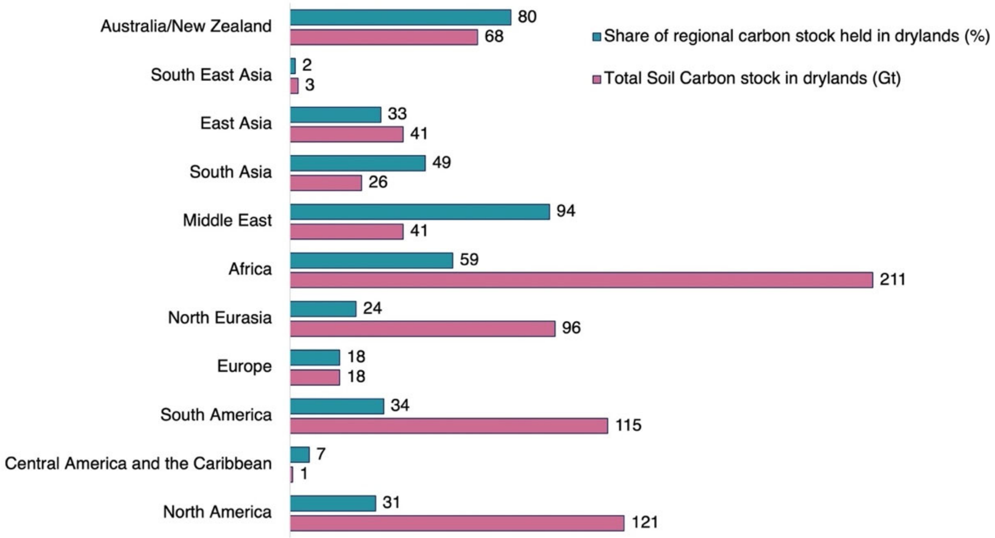

Figure 2. Comparison of total soil carbon stock in drylands (Gt) in different regions of the world and share of regional carbon stock held in drylands (%) (Graph created using data from [11]).

2. Methodological Approach

A systematic procedure was followed to ensure a good quality review of the literature on the SIC in dryland soils. First, using Web of Science, a comprehensive search of peer-reviewed publications (n = 2600) was followed based on the query: ((TS =) soil inorganic carbon) OR TS = (carbonate)) AND TS = (arid). Second, the reference section of each paper was critically studied to access additional papers (n = 3) relevant to this review topic. After removing duplicates (n = 543) using Mendeley Desktop, 2060 publications were screened based on their relevance to SIC in dryland soils. A total of 307 publications were assessed for eligibility to include in the review. Three main selection criteria were used during the eligibility section: (a) the publication must discuss the inorganic C in the soil system, (b) the publication must either discuss the factors affecting SIC and/or mechanisms involved in forming SIC and/or comparison between SIC and SOC, (c) the study must be conducted in a dryland ecosystem. A total of 72 papers were selected for review (Figure 3 and Table S1).

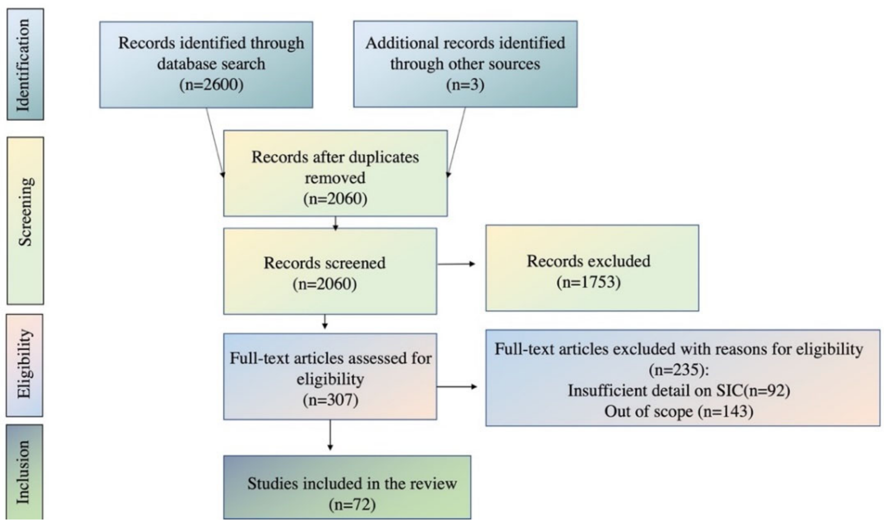

Figure 3. Flowchart of the methodologies followed for the review.

3. Distribution of Arid Soils and Their Soil Constraints

Approximately 41% of Earth's land surface is covered by arid and semi-arid areas [18] (Figure 4). Based on the aridity index, there are four major classes of arid lands: hyper-arid,

arid, semi-arid and dry subhumid [19]. Semi-arid regions are more extensive (15.2% of Earth's land surface), followed by arid regions (10.6%), dry sub-humid (8.7%), and hyper-arid (6.6%). Water scarcity, food scarcity, and harsh weather conditions are all common problems in dry regions [19]. Arid areas are characterized by high aridity (>70% aridity index), extreme temperature, high solar radiation, low and non-uniform distribution of rainfall, low humidity, and high wind velocity. Moreover, the soil is a sandy type with low water holding capacity, low organic C, and deficient in available nitrogen and phosphorus. Shortage of water, as well as the uneven distribution of available water, further restricts crop production and agricultural development in arid regions [20].

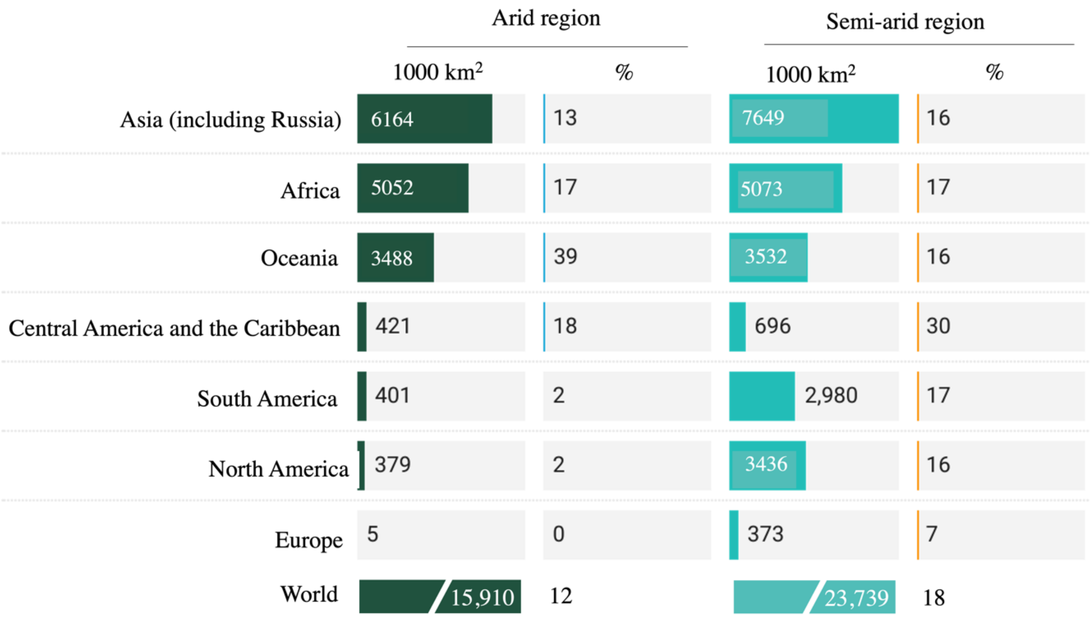

Figure 4. The regional extent of arid and semi-arid soils in different parts of the world (Modified from [19]).

4. Mechanism of SIC Formation in Dryland Areas

Not all arid regions are favorable for the formation of pedogenic carbonate. For example, the driest zones of the Atacama are too dry, which limits pedogenic inorganic C (PIC) formation [21]. Four conditions are essential for the formation of PIC [22]: (a) high soil pH (alkaline), (b) an active source of CO_2 in soil for HCO_3^- production, (c) a large amount of available Ca^{2+} and (d) an optimum level of soil moisture. In arid regions, SIC, particularly calcium (and magnesium) carbonates, are formed through the following two reactions [23]:

$$2CO_2 + 2H_2O \rightarrow 2HCO_3^- + 2H^+ \quad (1)$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2 \quad (2)$$

The development of calcium carbonates ($CaCO_3$) is influenced by soil CO_2, soil pH, soil moisture content, and soil calcium concentration [24]. High soil pH will result in the generation of HCO_3^- since a drop in soil H^+ will lead the reaction (1) to proceed to the right. Likewise, a decrease in pH or an increase in soil CO_2 content would cause a reaction (2) to shift to the left. The CO_2 consumed in carbonate formation is mainly derived from soil respiration, including autotrophic root respiration and heterotrophic microbial respiration. The majority of arid soils are non-flushing, where there is often less soil moisture to leach bicarbonate out of the soil profile [25]. Therefore, SIC stock may decrease in acidic soils due to the dissolution of carbonate, while an alkaline environment may provide the optimum environment for carbonate formation [4].

Many researchers have reported various formation mechanisms of PIC in arid and semi-arid soils [26,27]. Some have considered the abiotic mechanism of PIC formation in which the dissolved $CaCO_3$ crystallizes in low soil water content [28,29]. On the other hand, other researchers suggested the biotic mechanism of pedogenic $CaCO_3$ formation in which soil biota significantly influences $CaCO_3$ precipitation [30–34]. In the biotic process, soil organic matter (SOM) is predicted to play an important role in SIC formation in arid soils. SOM is derived from plant above-ground biomass, soil micro- and macro-organisms, and plant roots [35]. It is well known that SOM influences not only the soil enzyme activities but also the soil microbial activities [36]. Soil enzymes such as dehydrogenase activity (DHA) affect SOM decomposition and release of $CaCO_3$. Zhang et al. [37] showed a positive correlation between DHA, SOM, and $CaCO_3$. The above-ground plant parts can directly affect soil carbonate formation [38] because $CaCO_3$ content in the plant leaves can range from 0.4–1.06 mg cm^{-2} [30]. Furthermore, $CaCO_3$ can be found crystallized around root hairs [39].

The optimum pH of the soil to form secondary carbonate is 7.3–8.5 in the presence of Ca^{2+} in the soil solution [40]. PICs are formed through several mechanisms such as:

(a) The Per Descendum model: The dissolved carbonate from the upper profile leach down through the soil profile and re-precipitate in the subsoil [41].
(b) The Per Ascendum model: Ca^{2+} rises from the shallow water table through capillary movement and forms carbonates [42].
(c) The In situ model: The dissolution of carbonates is followed by re-precipitation near the bedrock [42].
(d) The Biogenic model: Secondary carbonates are formed through the activities of soil flora and fauna [32].
(e) Complex mechanisms: All the above-given mechanisms work simultaneously or in a sequential manner based on the prevailing environmental conditions [43].

5. SIC and C Sequestration in Dryland Soils

Why should we be concerned about SIC and C sequestration in dryland soils? Unlike a shift in SOC stocks, an increase in SIC content does not necessarily indicate atmospheric CO_2 sequestration [44]. Consequently, various scientists have questioned whether or not PIC precipitation is a C sequestration process [45–47]. The SIC literature is full of contradicting findings. There are three main SIC processes that affect the soil-atmosphere exchange of CO_2 in dryland soils [44].

(a) silicate mineral weathering

Two moles of CO_2 are consumed and produce bicarbonate during silicate weathering. However, the rate of silicate weathering is very slow (on the order of 50–500 mol Ca^{2+} ha^{-1} yr^{-1}) [48], which means only 0.001–0.01 t CO_2 ha^{-1} yr^{-1} will be consumed during the process [49]. Even if the rate of silicate weathering is accelerated, the subsequent C sink would still be inconsistent [44].

(b) carbonate dissolution

Carbonate dissolution is another SIC-related soil process that consumes CO_2 during a series of reactions. To consider carbonate dissolution a SIC sequestration process, the source and the fate of HCO_3^- must be known [44]. The CO_2 must be derived from soil respiration or decomposition of SOM. The HCO_3^- must be leached out from the soil profile and join the oceanic pool in which SIC is stored for thousands of years or even longer period. Otherwise, incomplete leaching of HCO_3^- from the soil profile leads to re-precipitation of carbonate in deeper layers of soil with the release of CO_2 and thus no net change in atmospheric CO_2 [50].

(c) Pedogenic inorganic carbonate formation

In arid and semi-arid areas, pedogenic carbonates are precipitated due to high evaporative demand and incomplete leaching of salts. The formation of PIC consumes two moles of HCO_3^- to precipitate one mole of $CaCO_3$ and release one mole of CO_2. The above natural reaction can be accelerated by irrigation. A clear description of inorganic soil C distributions and its controlling factors that leads to either C sequestration or loss as CO_2

will facilitate us in predicting the possible consequences of climate change on C cycling in arid and semi-arid areas.

6. Factors Affecting SIC Formation in Arid Soils

6.1. Climatic Factors

A growing body of research suggests that SIC may be just as dynamic as SOC [51–53]. Kim et al. [54] pointed out a potentially dynamic SIC pool that is sensitive to hydrological changes. SIC storage can be affected by a wide number of factors, including climate, land use, and soil characteristics (Figure 5). Precipitation, temperature, and other climate factors significantly affect the processes of evaporation and leaching, which in turn influence the dissolution and re-precipitation of carbonates (Figure 5). Raheb et al. [55] investigated the influence of climates on soil C pools under arid, semi-arid, and dry sub-humid conditions along a soil climosequence. With the increase in mean annual precipitation, total SOC and SIC storage increased from 3.75 and 6.28 kg m^{-2} under arid and semi-arid conditions, respectively, to 11.32 kg m^{-2} under dry sub-humid conditions. Although SOC was found to be low in arid soils, the ratio of SIC/SOC was the highest in arid regions. The high value of this ratio depicts the crucial role of climate on SIC storage as compared to SOC [55]. However, the time required for SIC storage was found to be higher in drier conditions as Raheb et al. [55] calculated the average time (in years) needed to store SIC in arid (26,000 years), semi-arid (23,100 years), and sub-humid conditions (15,400 years).

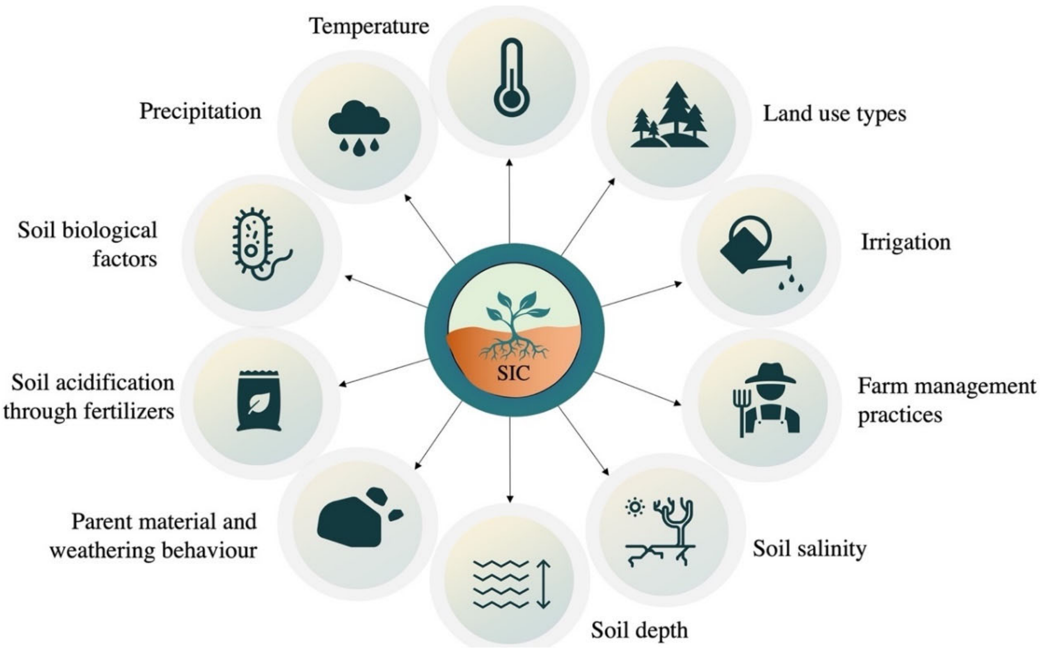

Figure 5. Natural and anthropogenic factors influencing the formation of soil inorganic carbon in dryland soils.

High evaporation: precipitation ratio inhibits carbonate dissolution and leaching, making arid soils rich in PIC [56]. According to Wu et al. [57], increasing aridity was associated with an increase in SIC content. This encourages the production and buildup of petrocalcic and calcic strata in arid places where there is little effective precipitation [45]. The humid circumstances, on the other hand, encourage a vigorous carbonate leaching process. Areas with annual precipitation of <500 mm have a greater concentration of SIC pool [45]. Mi et al. [58] revealed that 84% of China's total SIC pool was concentrated in locations with an annual rainfall of <500 mm. A total of 4.19 Pg C is also stored in areas with mean annual precipitation between 500 and 800 mm. In another study conducted by Tan et al. [59] in the Loess Plateau region of China, 84% of SIC stock was concentrated in the regions with an annual rainfall of <500 mm. There are two ways that mean annual precipitation could influence carbonate formation: directly by changing the $CaCO_3$ equilibrium solubility constant and indirectly by distributing precipitation inputs between leaching and evapotranspiration [60]. The seasonal drought period is the conducive time for precipitation of carbonates since both soil moisture and root activity are less during seasonal drought [12]. Additionally, elevation has a positive relationship with SIC due to its indirect effects on mean annual precipitation and mean annual temperature with increasing elevation [58].

6.2. Land Cover and Land Use

Due to changes in vegetation species and soil management approaches, land cover and land use types have a substantial impact on SIC content. Land-use changes from natural vegetation to cropland can rapidly induce the loss of SIC that has been stable for several years due to increased soil water fluxes [54]. SIC distribution patterns and stocks are also impacted by the vertical distribution of roots and SOC content in various land cover types [61]. Multiple biological parameters affecting the SIC pool can be altered by land use, including plant above- and below-ground biomass productivity, soil characteristics, and microbial processes [62]. Mi et al. [58] highlighted that the desert has the highest SIC, followed by grassland, farmland, marsh, shrubland, meadow, and forest. Through changes in C allocation, plant functional types could influence SIC distribution in deeper soil layers. Chang et al. [63] reported that the conversion of cropland to a forest in the central Loess Plateau led to the redistribution of SIC along the soil profile, but no increase in net SIC was observed. Jin et al. [64] found lower values of $\delta^{13}C_{SIC}$ in grassland than in the forest, indicating a greater generation of secondary carbonates in grassland than in the forest. SIC content and stock decreased during the conversion of cropland to grassland. During the tillage practices in grassland restoration, the SIC is vertically mixed, and further dissolution and leaching of carbonates to deeper soil layers might lower SIC during grassland restoration. However, the dissolution and leaching of SIC contribute to a little loss of SIC stock since restoration treatments significantly reduce surface runoff, which is one of the major causes of SIC loss [65]. Additionally, the rapidly growing plant biomass in a restored grassland takes up a considerable amount of Ca^{2+} in the soil and leads to a decline of Ca^{2+} in the soil. Moreover, the soil water content and high root biomass promote microbial activity and increase soil CO_2 production, leading to higher soluble SIC [58]. SIC formation is found to be more sensitive in sandy soil than the clayey type of soil [66].

Other land-use studies in dryland soils reported a higher contribution of PIC to SIC in croplands than in grasslands [67]. Several authors have reported a high rate of SIC sequestration of 0.02 Mg C ha^{-1} $year^{-1}$ under natural vegetation and up to 0.4 Mg C ha^{-1} $year^{-1}$ in managed lands [68]. Murty et al. [69] indicated that in temperate and tropical conditions, conversion of grassland to agricultural land had increased CO_2 emission with a decrease in soil C stock. Zhao et al. [70] found relatively higher SIC under the shrub cover than in forests and grassland. The larger quantity of PIC under the shrub cover is due to more Ca produced from litter under shrub cover, higher soil microbial biomass, and slow transfer of PIC owing to low soil water content under shrub cover. This indicates that shrubland is one of the best vegetations for the fixation of inorganic C in the soil.

Intensive cultivation practices such as deep tillage disturb the soil and break down soil aggregates [71]. Moreover, plant-derived C inputs to soil are generally less in farmland, thus affecting the dissolution and precipitation of SIC. Therefore, in general, cultivation leads to a decrease in SIC, and restoration of cropped lands could significantly promote SIC storage [72]. However, it is not necessarily true in all cases since carbonate precipitation or dissolution largely depends on soil pH and Ca^{2+}/Mg^{2+} source. Soil pH and source of Ca^{2+} or Mg^{2+} control SIC and its precipitation, respectively [73]. Other researchers showed greater accumulation of both SOC and SIC stocks in agricultural than in non-agricultural lands under arid and semi-arid conditions, e.g., in the middle of the Hexi Corridor, Gansu, China [74], around the Yunwu Mountain, Ningxia, China and other parts of China [75], and in the Russian Chernozems [76] and Loess soils of Russia [77].

Wu et al. [57] reported that 51% of total cultivated soil in China showed SIC loss at the rate of 0.5–4.0 kg C m^{-2}, from the 1980s to 2008, especially in paddy fields, irrigated farms, and dry farmland. Irrigation practices coupled with the application of acidifying fertilizers increase the loss of SIC from soil profile [78]. The carbonate weathering and erosion are further increased through agricultural practices by exposing the calciferous horizon to the soil surface [45]. On the other hand, an increase in SIC was observed in irrigated silty soils, irrigated desert soils, seirozems, and black soils [57]. Irrigation in arid and semi-arid soils increases plant biomass production, thus increasing plant respiration and microbial decomposition of SOM, releasing CO_2 [45]. The elevated CO_2 leads to increased weathering [29] and promotes the consumption of atmospheric CO_2. Another probable reason is the external addition of Ca^{2+} and Mg^{2+} from irrigation water or the addition of fertilizer and manure that increases carbonate formation [71]. However, when such irrigation water is applied to arid non-alkaline soil where groundwater contains a high bicarbonate concentration, CO_2 is released during carbonate precipitation [29]. These discrepancies complicate our comprehension of the effect of land use changes on SIC or SOC dynamics in arid and semi-arid environments. Such inconsistencies between SIC stock and land use systems may also highlight the intricate interaction between climate, land management, and soil conditions and the formation of carbonates in arid soils [79].

6.3. Farm Management Practices

Farming practices such as intensive cropping, irrigation, residue, and fertilizer application/management may also increase SOC stock in agricultural lands, which leads to enhanced CO_2 production and ultimately increased SIC stock [57]. Higher SIC density in agricultural land than in other land uses [80] may be due to the increased availability of Ca^{2+}/Mg^{2+} associated with irrigation and fertilization [81]. To enhance carbonate accumulation in the soil profile, it is also essential to increase soil fertility. Wang et al. [81] demonstrated significant enhancement of carbonate accumulation (especially in subsoil) with the application of organic amendments in the cropland of North China. These results were also supported by Zhang et al. [82], who reported an increased SIC stock in fertile soils than in low fertile loess soils of the Lanzhou area, China. Few long-term experiments reported a varying contribution of PIC to SIC (29%–89%) [68,81,82], which indicates the possible major influence of crop management practices on SIC formation. Although, there is limited literature on pedogenic inorganic carbonates (PIC) contribution to SIC. In fact, intensive cropping may enhance PIC formation, and therefore, proper agricultural management is also essential to increase both the SOC and SIC storage in arid soils [5]. Thus, in order to understand SIC variability, it is important to study PIC dynamics in various soil types. Intensive tillage practices expose the calciferous horizon to the soil surface, thereby increasing carbonate weathering [45]. The possible fate of the SIC can be either it is leached down to deeper soil layers or has converted into bicarbonate that is further transported to groundwater or joined the river surfaces or lakes and ultimately to the ocean [83]. For example, the Yellow River across northern China has been experiencing an increase in dissolved Ca^{2+} and inorganic C over the past 40 years [84].

6.4. Irrigation

In croplands, irrigation has more pronounced effects on SIC losses than tillage or fertilization [54]. SIC studies under long-term irrigation have shown mixed results: SIC increases in irrigated treatment [47,57], null effect on SIC [85], and SIC increases only in limited irrigation [86]. Greater water content not only acts as a medium for dissolution and transport of carbonates but also allows SIC to rapidly re-equilibrate with CO_2 present in soil pores [87]. The greater loss of SIC in irrigated cropland through carbonate dissolution is due to increased reactive area of dampened finer laminar coating of disseminated carbonates under croplands [56]. However, it is equally important to understand whether this SIC mobilization indicates a net C source or sink. The majority of irrigation water in such arid regions contains up to 1% dissolved CO_2 [88]; increasing this concentration can accelerate the rate of carbonate production [29]. Due to high solar radiation in arid regions, irrigation water is typically warmer than groundwater [47]. The solubility of CO_2 at 0 °C, 25 °C, and 400 °C is 0.02, 0.03, and 0.08 molL^{-1}, respectively [29], demonstrating the solubility of CO_2 in irrigation water is significantly temperature sensitive. When irrigation water reaches a field, its temperature can climb to as high as 2000 °C and is further elevated when it comes into touch with the soil surface on hot days. The higher temperature of irrigation water increases the response time and, under favorable conditions, may increase carbonate precipitation. In addition, as irrigation water runs through canals and agricultural fields, dissolved cations can cause its pH to rise. The high pH of the irrigation water may also promote SIC formation. Entry et al. [47] reported that there is a greater possibility of a higher potential amount of SIC sequestration if irrigated areas are enlarged, and land use patterns are altered.

Irrigation in arid areas is advantageous for SIC accumulation. Irrigating with Ca^{2+}-rich water favor bicarbonate formation and an increase in SIC. It also helps in the redistribution of SIC to deeper soil layers. The increase in SIC in irrigated land as compared to rainfed soils is attributed to the dramatic increase in plant biomass production [57]. High biomass production enhances plant respiration and SOM decomposition, thus increasing soil CO_2 levels [45]. Higher soil CO_2 favors increased carbonate weathering and consumption of atmospheric CO_2 [29]. Irrigated soils showing a decrease in SIC is primarily due to high leaching and maintenance of high water content at the soil surface, which is responsible for elevated CO_2 concentration and greater dissolution of soil carbonates [89]. Efficient irrigation with leaching less than 30% of the applied water could favor carbonate accumulation in semi-arid and arid regions.

6.5. Soil Acidification through Fertilizers

A decrease in SIC in topsoil in croplands might possibly be due to a drop in soil pH linked to soil acidification from the application of chemical fertilizers [90]. The decline in soil pH will aid in the dissolution of soil carbonate and low SIC content. According to recent studies, fertilizer may increase soil acidity and cause soil carbonate to dissolve [56,91]. Soil acidification is one of the major global threats to the sustainable development of ecosystems [92] because a change in soil pH can regulate both the SOC and SIC dynamics. Although soil acidification is a natural process, it is accelerated by anthropogenic activities such as the long-term overuse of nitrogen fertilizers [93].

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \tag{3}$$

$$\text{Organic C} \rightarrow RCOOH \rightarrow RCOO^- + H^+ \tag{4}$$

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^- \tag{5}$$

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \tag{6}$$

The change in soil pH in calcareous soil could be explained through three processes:

(a) Equations (3) and (4) depict the release of proton ions through nitrification and soil organic matter decomposition, respectively [70].
(b) Equations (5) and (6) depict the consumption of H^+ ions during the dissolution of SIC, thus releasing CO_2 [94].
(c) Leaching of dissolved inorganic C to groundwater [95].

The application of nitrogen fertilizer can reduce soil pH and alter the C balance in calcareous soils and promote acidification in soils [96]. In Equation (3), it is shown that with one mole of nitrate produced, two moles of H^+ ions will be generated under aerobic conditions [97]. These protons are neutralized by SIC in calcareous soils [90]. Therefore, a lower soil pH in calcareous soils leads to a decline in SIC [96,98]. If the soil is limed, SIC will be released faster than the C from SOC [99]. In addition, although fertilizers are applied in topsoil, they can still cause soil acidification in deeper soil layers through the movement of protons, which is expected to induce SIC loss in the deeper soil layer [92].

SIC lost through degassing depends on the type and amount of fertilizers applied in the soil. Long-term application of nitrogen fertilizers causes agricultural acidification at a rate of 30–240 kmol H^+ ha^{-1} $year^{-1}$, leading to a maximum loss of 0.36–2.8 Mg C ha^{-1} $year^{-1}$ [90,100]. Soil acidification is generated by nitrate leaching, removal of alkalinity during crop harvest, accelerated nitrogen fixation by legumes, and the application of ammonium-based fertilizers [101,102]. Soil acidification rates of 10 kmol H^+ ha-^{1} yr^{-1} were found in highly exploitative agricultural soils [103]. This can be partially offset by accelerated calcite dissolution in calcareous soils, creating a potential net C sink on the order of 0.03–0.12 t C ha^{-1} yr^{-1} if all of the $HCO^-{}_3$ leached down the soil profile and join a long-lived reservoir [44].

6.6. Temperature

Temperature is another important factor that governs SIC storage in an arid region. An increase in global temperature could alter the dissolution of carbonate directly or indirectly through the products of SOC decomposition [4]. With the increase in temperature, the solubility of CO_2 in water decreases, affecting the solubility of carbonates [104]. For example, Buysse et al. [105] reported greater CO_2 emissions (due to greater CO_2 solubility) from limed farmland soils at 5–15 °C than 15–25 °C. On the other hand, in an incubated study, Ahmad et al. [4] contradicted and reported a 59% increase in CO_2 emissions from limed soils when the temperature increased from 20 °C to 40 °C. Surface reactions and mass transfer could be influenced by higher temperature, which further leads to higher carbonate dissolution and C release from soil carbonates. The increase in temperature also accelerates the supply of protons (through nitrification and/or humification) and the rate of lime dissolution. Higher temperature during the plant growing season also increases the release of CO_2 from the rhizosphere due to higher soil respiration. The increased rate of proton release in the rhizosphere affects the soil pH and further increases carbonate dissolution. The temperature sensitivity of carbonate dissolution must be further studied to understand the effect of climate change on SIC sequestration.

6.7. Microbial Soil Factors

While most researchers considered the main mechanism of PIC formation as an abiotic process, some have identified the role of soil (micro) organisms in inducing $CaCO_3$ precipitation [37]. Any biotic factors that affect the deposition rate of SOM also influence soil $CaCO_3$ content [106]. Due to more soil microbial biomass, the unstabilized SOC is mineralized to produce more CO_2, which further dissolves in the soil solution and forms carbonates, which later precipitate to $CaCO_3$ in the presence of Ca released from the decomposed litter. This reaction sequesters one mole of CO_2 to form one mole of PIC. On the other hand, high soil microbial biomass also means higher production of CO_2 since half of the soil respiration is derived from microbial respiration [70]. The higher partial pressure of CO_2 could promote the dissolution of PIC in the topsoil layer, which later becomes distributed to deeper soil layers and re-crystallizes under low soil water content. This process neither generates nor consumes CO_2 [70].

6.8. Soil Depth

While assessing SOC and SIC stocks in desert soils, including shrub soils and agricultural soils, SOC showed a decreasing trend with an increase in depth, whereas the opposite trend was observed in the case of SIC. One of the most prevalent errors in C sequestration research under arid conditions is focusing solely on changes in soil total organic C at the surface (e.g., 0–20 cm depth) because sampling and data collection are relatively simple [107]. However, in shrublands, Jobbágy and Jackson [108] found that the relative distribution of SOC was significantly deeper in arid conditions (0–250 mm yr^{-1}) than in semi-arid conditions (250–500 mm yr^{-1}), while no such difference in the vertical distribution of SOC was observed in grasslands regardless of climates. This trend might be attributed to the fact that in arid shrublands, the relatively deep root system of the shrubs may lead to deeper soil C profiles than in arid grasslands [108].

Xie et al. [109] also reported the downward leaching of soil C containing water when dry areas are irrigated sufficiently. The amount of irrigation water used in dry areas influences the depth of water movement and thereby affecting the rate of inorganic C transportation throughout the soil profile. Higher SIC levels are formed in deeper soil layers, even below 2 m in the loess soil [75]. Therefore, the depth of the soil layer is one of the major factors in determining the profile distribution of inorganic C in saline/alkaline areas [79]. Management practices that increase soil erosion remove more weathered surface soils. While SIC is generally found in deeper soil layers, eroded soils show an increase in SIC in surface soils [89]. Approximately 80% of SIC is captured below 1 m, and 50% is stored below 3 m [79].

6.9. Parent Material

The parent material and its weathering behavior are other aspects that influence SIC formation [110]. For example, high SIC content in the Loess Plateau of China is associated with the primary aeolian deposit rich in $CaCO_3$ [57]. Basalt weathering is crucial in the terrestrial C cycle because it exposes H^+ (dissociated from H_2CO_3) and releases Ca^{2+} and Mg^{2+} cations, which combine with bicarbonates to form carbonates in soil [111]. Therefore, pedogenic forms of SIC are found in soil with carbonate-free parent rocks. In arid and semi-arid regions, PIC can also be accumulated in non-carbonate parent materials through the reaction of Ca^{2+} ions with water (from rainfall) and CO_2 (derived from plant root respiration) [112]. Because the weathering rate of parent materials increases with the temperature only in the presence of water, the weathering rate in arid regions is slow.

6.10. SIC in Salt-Affected Soils

Salt-affected soils tend to dominate in arid and semi-arid regions. Generally, owing to the poor soil's physical and chemical properties and harsh climate, the plant productivity in salt-affected soils is generally poor. This leads to low plant biomass and lower inputs of organic materials, and low SOC. On the other hand, SIC levels can be high in salt-affected soils and are attributed to the high soil pH and high soil Ca^{2+} and Mg^{2+} that can enhance carbonate precipitation [113]. Schlesinger [114] reported poor SIC exchange with the atmosphere, as low as 1.0–5.0 g C $m^{-2}yr^{-1}$ in the desert soils. However, it could also be as high as 62–622 g C $m^{-2}yr^{-1}$ in salt-affected soils [53]. Sodic soil reclamation can both reduce or favor SIC accumulation in the soil [89]. With the application of gypsum to alkaline or sodic soils, the Ca precipitates the soluble bicarbonates and carbonates in the soil, resulting in an increase in SIC. On the other hand, green manuring and the application of sulfur and sulphuric acid tend to elevate CO_2 concentration in the soil resulting dissolution of carbonate. Widespread use of acids to prevent emitter clogging in drip irrigation also removes a significant amount of carbonates within 10–20 years and for soils with <3% carbonates [89].

7. Relationship between SIC and SOC in Dryland Soils

The relationship between SIC and SOC processes in arid soils is another source of complexity of SIC dynamics in arid soils. The SIC–SOC relationship in croplands could be either positive [80], negative [70,82], or null [5]. In surface soils of North China Plain [115] and west Loess Plateau [116], negative relationships were found between SOC and SIC, whereas positive relationships between SIC and SOC in arid areas were established by Su et al. [74] in the Badan Jaran Desert, Gansu (0–30 cm depth) and Wang et al. [81] in the Yanqi Basin, Xinjiang (0–100 cm depth). Guo et al. [90] also found a significantly positive correlation between SOC and SIC in the cropland of North China Plains, suggesting the increasing SOC might lead to an increase in SIC stocks. SIC and SOC showed a significant positive correlation in croplands [80,90] shrub land [37,74] and afforestation soil [18,67]. The quality of irrigation water during cultivation strongly affects the SIC content in the soil.

For example, irrigation with alkaline pH water, the presence of alkaline parent material, and the application of alkaline fertilizers such as urea supplied the opportunity for carbonate precipitation in the Qinghai–Tibetan Plateau, Northern China [96]. On the other hand, due to increased plant biomass in restored cropland, the soil pH declined, accompanied by greater water retention promoting dissolution of SIC. The Ca^{2+}/Mg^{2+} rich soils in croplands of Northern China, because of long-term and extensive application of Ca^{2+}/Mg^{2+} rich fertilizers and irrigation water, not only promotes SIC precipitation but also aids in consuming CO_2 from the atmosphere through soil calcification. Dissolved SIC could be lost to the atmosphere as CO_2 or transferred to another region through soil erosion and runoff, or redistributed into the deeper soil layers [96]. Therefore, the net decrease in SIC in grassland could be due to release to the atmosphere or redistribution of SIC along the soil profile since vegetation recovery reduces the surface runoff and erosion. Moreover, increased root biomass lowers soil pH and inevitably decomposes a part of total carbonate, and releases CO_2.

Soil pH could play an important role in maintaining the relationship between SIC and SOC under arid conditions [80]. Decomposition of SOC and high root respiration releases more CO_2 into soil, thus creating acidic conditions in soil [80]. The low soil pH favors the dissolution of carbonate and thus results in a negative relationship between SOC and SIC in the surface layer [117]. Therefore, a positive relationship could be predicted in soils with higher pH and without Ca/Mg limitation [80]. The increasing acidity of soils with high amounts of SIC leads to a significant decrease in carbonate formation [96], indicating SIC as a dynamic rather than stable C pool. Therefore, soil acidity could influence the C sequestration process through sedimentation of carbonates or the release of CO_2 into the atmosphere.

The discrepancies found in the relationship between SIC and SOC indicate that both SIC and SOC might respond differently to the changes in environmental conditions. For example, soil salinity restricts the accumulation of SOC due to the low stability of SOC in high soil pH. On the other hand, it increases Ca^{2+}/Mg^{2+} concentration in the soil and promotes SIC accumulation, thus generating a negative relationship between SIC and SOC [118]. Under high soil moisture coupled with high soil pH, desorption of dissolved organic C and SIC dissolution increases, thus showing a positive relationship between SIC and SOC [119]. Additionally, a high concentration of $CaCO_3$ improves soil aggregation and increases SOC stabilization [120]. Shi et al. [121] did not observe any significant relationship between SOC and SIC in the top soil but showed a positive relationship within 0–100 cm soil depth in croplands of North China Plain. Interestingly, Guo et al. [90] estimated a positive relationship between SOC and SIC in the same study area. These contradictory findings indicate the relationship between SOC and SIC is complex, which may be a result of the decoupling of multiple processes associated with carbonate formation over time and space. Higher SOC content releases a high concentration of CO_2 in the soil, leading to more production of H^+ and HCO_3^-. High levels of H^+ help in the dissolution of carbonate, and thus, a negative relationship exists between SOC and SIC. On the other hand, the higher production of HCO_3^- will favor the precipitation of SIC and generate a positive relationship [80]. Therefore, a negative relationship is generally observed in topsoil of cropland and grassland where SOC is high [95]. Higher CO_2 production reduces soil pH and leads to the dissolution of carbonates. However, it is always not true. Soils with high pH (>8) have a high buffering capacity that even after the high production of CO_2, the resulting soil pH is still alkaline, showing a positive relationship [121].

8. Dissolved Inorganic Carbon (DIC) as a "Missing Sink" in C Sequestration Studies

Although the global C balance includes a large C sink in the terrestrial ecosystem, it is difficult to fully identify the potential of each terrestrial C sink and understand its mechanisms [122]. In a few recent findings, a part of the "missing C sink" could be explained by the removal of atmospheric CO_2 through desert soil, capturing CO_2 at a magnitude of approximately 100 g C m^{-2} yr^{-1} [123]. However, it has caused many controversies as a similar magnitude of C has not been observed in terrestrial ecosystems [25]. Li et al. [124]

discovered a potentially large C sink in irrigated saline/alkaline desert regions. Through conventional radiometric analysis, Li et al. [124] identified DIC, which was retained neither in the plant nor in the soil. The DIC was leached out from the irrigated arid soils and deposited in the saline or alkaline aquifers in deserts under sparse vegetation cover.

The origin of DIC is from the dissolution of CO_2 released from soil respiration into the soil solution of irrigated saline or alkaline soil [125]. It is then transported downward into the groundwater aquifers [123]. Kessler and Harvey [126] reported the average C input rate as 1.34 g C m^{-2} yr^{-1} but lower in the case of arid soils in the Tarim Basin. The DIC sequestration rates in irrigated saline or alkaline arid soils can be even greater than 20 g C m^{-2} yr^{-1} which is 1–2 orders of magnitude greater than earlier reported [124]. The DIC is regarded as a hidden, untouched inorganic C pool in saline or alkaline aquifers in desert areas. Arid areas are defined by higher evaporation than precipitation, thereby increasing soil salinity or alkalinity. One of the generally recommended practices to reduce soil salinity is over-irrigation, where good quality irrigation water is applied more than the crop requirement to leach away the salts [127]. Lindsay [128] stated that the solubility of CO_2 increases linearly with electrical conductivity and exponentially with the pH of the soil solution. Therefore, it is obvious that in arid saline/alkaline water, the CO_2 solubility will be much higher than that of pure water, thus containing a high amount of dissolved CO_2 or DIC in saline/alkaline aquifer.

Sources of water, such as rainfall and glacier, are nearly C free. However, as it flows into rivers of a mountain, it contains a considerable amount of CO_2. However, the DIC content in the groundwater leached out from the saline/alkaline soils is more than twice that of the irrigation water [124]. These findings might not be applicable where good quality irrigation water is not available for over-irrigation. One of the major problems associated with these findings is the quantification of DIC sink strength and its size. This is due to the fact that in order to estimate sink strength, it is necessary to understand the recharge rate of groundwater, which still remains a challenge in hydrological research [129]. Secondly, different factors of soil influence CO_2 solubilities, such as salinity/alkalinity of soil [130], rate of root respiration [131], and soil temperature [130], which are season- and time-dependent. The large spatial and temporal variability also affects the feasibility of DIC quantification in leaching water. Despite all these findings, over-irrigation and leaching of groundwater in arid saline/alkaline soils do not necessarily depict the creation of a C sink as this hidden C may be released back into the atmosphere if it is discharged into rivers, lakes, and streams.

9. Inorganic C Fluxes in Dry Land Systems: Their Role in Gaseous Ecosystem C Flux

In spite of the widespread distribution of arid soil, little attention has been paid to estimating the C fluxes in arid soils and ecosystems under prolonged dry periods. Multiple studies have mentioned potential abiotic implications on net CO_2 exchange, starting with Emmerich's [46] study on the behavior of CO_2 fluxes across high-carbonate soils. Large daily CO_2 emissions were detected in the summer in combination with rain events, as determined by long-term CO_2 flux measurements in the New Mexico Chihuahuan desert [132]. An abiotic CO_2 source (the dissolution of carbonates) might be responsible for some of the CO_2 emissions. As shown by Inglima et al. [133], in a carbonate Mediterranean ecosystem, SIC release accounts for 40% of the total soil CO_2 flux when soil moisture levels are low. Rain events led to a decrease in the relative inorganic contribution as a result of a significant increase in the organic flux. Large magnitudes of CO_2 uptake have been recorded, both from soil chambers in the Gobi Desert [134] and also with open- and close-path eddy systems in the Mojave Desert [52], including net C uptake even at night. Stone [17] highlighted these two articles to argue that arid ecosystems may be the long-sought-after C sink. Although there are numerous hypotheses on the abiotic mechanisms involved in such CO_2 uptake, the actual mechanisms remain still unknown [25].

Here are the main findings from a few studies on soil CO_2 fluxes in dryland ecosystems:

(a) In the Chihuahuan Desert, soil CO_2 profiles and fluxes, as well as volumetric soil moisture and temperature, were recorded by Hammerlynck et al. [135] throughout a three-month hot and dry period in both bare interplant canopy soils and under plant canopies. The results indicated that elevated CO_2 might directly affect abiotic C dynamics in the dry season. Even if temperature and precipitation have no effect on the dynamics of soil CO_2 and temperature, increasing atmospheric CO_2 will speed up nocturnal carbonate dissolution. This could result in more carbonate dissolution and soil uptake beneath the canopy. Increasing levels of CO_2 could alter the spatial and temporal patterns of PIC development during warm, dry seasons.
(b) To explore how climate influences the CO_2 fluxes and C balances in soil by interacting with biotic drivers, Ball et al. [136] measured soil CO_2 flux in experimental field manipulations, microcosm incubations, and across natural environmental gradients of soil moisture and found that CO_2 flux in dry valley soils is driven primarily by physical factors such as soil temperature and moisture, suggesting that future climate change may alter the dry valley soil C cycle. This shows the potential for arid polar soils to absorb CO_2, mostly driven by abiotic factors related to climate change.
(c) Soils rich in carbonaceous parent material are associated with CO_2 exchange patterns that cannot be explained by biological processes, such as asymmetric daytime outgassing or nighttime CO_2 uptake during times when all vegetation is senescent. Carbonate weathering reactions cannot account for either of these events because the rates of CO_2 exchange are too low. By imposing ventilation-driven CO_2 outgassing in a carbonate weathering model, Roland et al. [137] showed that carbonate geochemistry is accelerated and plays a substantial role in a semi-arid ecosystem's CO_2 exchange pattern. Ventilation depletes soil CO_2 during the day, disrupting carbonate equilibria and accelerating carbonate precipitation and CO_2 generation. At night, ventilation stops, and CO_2 levels rise steadily. Increased carbonate dissolution consumes CO_2 and compensates for increased daytime precipitation. This is why only a minimal effect on worldwide carbonate weathering rates is expected.
(d) Pedogenic carbonate formation occurs when the soil is warm and extremely dry, not during the mean growing season, as is commonly believed [138].
(e) Roby et al. [139] investigated the ways in which soil temperature, soil moisture, and gross ecosystem photosynthesis control soil CO_2 flux in semi-arid ecosystems. Including soil moisture and gross ecosystem photosynthesis in the models of soil CO_2 flux can help reduce the amount of uncertainty in semi-arid ecosystem C dynamics.
(f) A large carbonate pool exists in arid soils, which may contribute to surface-atmosphere CO_2 exchange via a diurnal cycle of carbonate dissolution and exsolution. Abiotic processes have a significant role in the C cycle of desert soils. Soper et al. [140] demonstrate that diurnally evolving CO_2 occurs in part from carbonate sources, providing a source to balance the nocturnal CO_2 uptake found in arid areas and likely maintaining the system at (or close to) C equilibrium.
(g) Kowalski et al. [141] tested the idea that surface-atmosphere CO_2 exchanges in terrestrial ecosystems can always be explained by biological processes alone, without considering geochemical cycling by karst systems. Further, large daytime CO_2 emissions during prolonged drought and plant senescence contradict ecophysiological explanations. CO_2 emissions in the afternoon during the summer in a temperate pasture above an accessible cave are hard to explain biologically, but they occur at the same time as cave ventilation. These studies reveal that CO_2 exchanges between the atmosphere, ecosystems, and carbonate substrates are occasionally related directly.
(h) Based on isotope analysis, the SIC pool adds significantly to soil CO_2 and, in turn, to the average CO_2 outflow [142]. This contribution was season and location sensitive. During daily cycles, the inorganic source contributed significantly to soil CO_2, with the largest levels occurring during the day in tandem with the maximum respiration rates.

10. Conclusions

This review highlights that SIC is the main form of soil C in arid and semi-arid regions; desertification could affect SIC content in many parts of the world. Soil C dynamics in dry and semi-arid ecosystems must be considered to comprehend the global C cycle and assess terrestrial ecosystem responses to rising global temperature. The theory of 'missing sink' hidden underneath the deserts must be studied further in areas where irrigation is a major issue, or good quality irrigation water is not available. The chemistry of SIC and its interaction with SOC in arid regions must be understood/identified clearly. If the focus of study needs to shift from SOC to SIC in arid soils, the C sequestration potential of SIC in arid soils must be studied under different soil types and land use system/management practices under diverse climatic conditions. Future detailed studies must be conducted on the use of stable isotopes of C and O to demonstrate the origin of pedogenic carbonate minerals and how this relates to land use change. In addition, there is also a need for an in-depth understanding of soil management and fertilization, including liming of acidic soils on mineralization of native soil C and geochemical solution modeling to predict the stability of calcite in arid regions. Finally, this review highlights the need for generating information on SIC potential in C sequestration, which can definitely form a part of climate change mitigation strategies in arid soils and it will also assist policymakers and researchers make land-use and soil-management decisions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agriculture12081256/s1, Table S1: Important studies included in the review.

Author Contributions: Conceptualization—S.J., A.N., R.C.D. and R.L.; writing—original draft preparation, A.N. and S.J. writing—review and editing, R.C.D., R.L., C.S.R., A.P., A.N. and S.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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