

Sequestration of atmospheric CO₂ in global carbon pools

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Received 4th June 2008, Accepted 24th June 2008

First published as an Advance Article on the web 3rd July 2008

DOI: 10.1039/b809492f

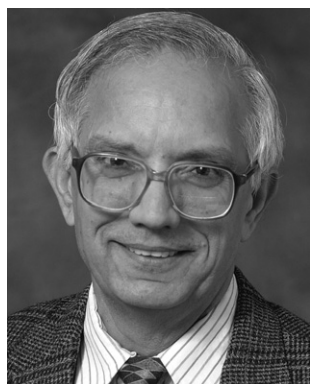
Sequestering atmospheric CO₂ is necessitated by its present concentration of 385 ppm and increasing at the rate of 2 ppm y⁻¹. Increase in atmospheric emission of CO₂ with the attendant global warming and environmental degradation are driven by global energy demand. In comparison with the emission of 300 Pg C between 1850 and 2000, total emission during the 21st century is estimated at 950 to 2195 Pg, with an annual rate of emission of 20 to 35 Pg C y⁻¹. Reduction of CO₂ atmospheric loading can be achieved by biological, chemical and technological options through either reducing or sequestering emissions. This article describes technological options of sequestering atmospheric CO₂ into other global pools. Geologic sequestration involves underground storage of industrially emitted CO₂ into the geosphere for long-term and secure storage. Liquefied CO₂ is injected about 1000 m below the ground surface either in stable porous rocks, oil wells, coal beds, or saline aquifers. Co-injecting CO₂ along with H₂S and SO₂ is also possible. Over time, the trapped CO₂ reacts with minerals to form carbonates, enhances oil recovery, or displaces coal bed methane. Deep injection of CO₂ under the ocean creates a CO₂ lake which eventually penetrates into the sediments. Iron fertilization is another technique of enhancing the C pool in marine biota, notably phytoplankton. The so-called “biological pumping” is based on the “iron hypothesis” of transferring C to the ocean floor. Terrestrial C sequestration is based on the natural process of photosynthesis. Transfer of CO₂ into the biotic pool and soil C pool *via* humification and formation of secondary carbonates has numerous ancillary benefits through enhancement of ecosystem services. Soil C sequestration is essential to improving soil quality, increasing use efficiency of agronomic input, and advancing world food security. It is also needed to improve water quality by filtration and denaturing of pollutants, and enhancing biodiversity by saving land for nature conservancy. Soil C sequestration is a low hanging fruit, and a bridge to the future until low-C or no-C fuel sources take effect.

I. Introduction

Three important and inter-related global issues of the 21st century are: (i) atmospheric concentration of CO₂ at 385 ppm in 2008 (+37.5% compared with the pre-industrial level of 280 ppm) and increasing at the rate of 2 ppm y⁻¹ (0.52% y⁻¹) with the attendant impact on the current and projected global warming, (ii) world annual energy use of 500 EJ (Exajoule = 10¹⁸ Joules, 1

Quad = 10¹⁵ BTU = 1.05 EJ), increasing at the rate of 2.2% y⁻¹ and projected to be 537 EJ by 2010, 590 EJ by 2015, 637 EJ by 2020, 687 EJ by 2025 and 737 EJ by 2030,¹ and (iii) food—insecure population of about 1 billion and increasing because of an increase in price of energy and the related input (*e.g.*, fertilizer, irrigation), decline in per capita arable land area (caused by conversion to urban/industrial uses and increasing susceptibility to soil degradation), and reduction in per capita availability of renewable fresh water resources for agricultural use. Increasing energy demand is a major cause of CO₂ emission. Fossil fuel combustion for energy production emits between 0.14 to 0.28 Mg C Mwh⁻¹ of energy.² Thus, fossil fuel combustion and other anthropogenic activities have strongly impacted the atmospheric enrichment of several greenhouse gases (GHGs) with the attendant impact on climate change. Relative emission of GHGs comprises 79.9% energy-related CO₂, 9.5% CH₄, 5.8% N₂O, 3.0% non-energy CO₂ and 1.8% other gases (www.climate-technology.gov). With regards to the energy budget of the Earth, however, radiative forcing or the global warming potential of different GHGs must also be considered. Therefore, mitigating the increase in atmospheric abundance of CO₂ necessitates identification of options which: (i) reduce emissions by using low-carbon or no-carbon fuel sources, (ii) enhance energy use efficiency by minimizing losses, and (iii) sequester atmospheric CO₂ into other reservoirs with secure storage and long residence time. With increasing reliance on fossil fuel as the dominant energy source

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for most of the 21st century, disposal of CO₂ by engineering, chemical and biological techniques is important to reducing the atmospheric loading and minimizing the risks of climate change. Total emission of C, with business as usual during the 21st century, is estimated at 950 to 2195 Pg compared to only 300 Pg emitted between 1850 and 2000.³ The rate of annual emission by 2100 is estimated at 20 to 35 Pg C y⁻¹ compared with the 1990 baseline emission rate of only 5.5 Pg y⁻¹.³ It is thus imperative that the anthropogenic emissions of CO₂ be sequestered in other global pools for long-term and secure storage. This article collates and synthesizes research information, and describes technological options of C sequestration to off-set anthropogenic emissions due to fossil fuel combustion, land use change and other activities to stabilize the atmospheric concentration of CO₂ at a desired level (e.g., 550 ppm).

II. The global carbon cycle

The five global C pools are interconnected (Fig. 1), and the flux among these pools is strongly influenced by anthropogenic perturbations. The gross primary production ranges from 90 to 130 Pg C y⁻¹ (mean of 120 Pg C y⁻¹), which is balanced by plant respiration of 40 to 60 Pg y⁻¹ and decomposition of soil organic matter (SOM) of 40 to 68 Pg C y⁻¹.⁴ The anthropogenic emissions involve two principal components: fossil fuel combustion of >7.5 Pg C y⁻¹ during 2000 s and land use conversion (deforestation) and soil cultivation of about 1.6 Pg C y⁻¹.⁵ Total anthropogenic emissions of about 9.1 Pg C y⁻¹ are balanced as follows: (i) retention in the atmosphere by 4.1 Pg C y⁻¹ (45%), uptake by ocean by 2.5 Pg C y⁻¹ (27.5%), and absorption by an

unidentified terrestrial sink by 2.5 Pg C y⁻¹ (27.5%). It is argued that the capacity of the land-based sink may be decreasing.⁶

For assessing whether the terrestrial biosphere is a net C sink, it is relevant to know its C budget at different spatial scales and its sink capacity. Ruddiman^{8,9} observed that the terrestrial C pool has been a source of the atmospheric CO₂ ever since the dawn of settled agriculture about 8000 to 10 000 years ago and of CH₄ since cultivation of rice paddies and domestication of livestock about 5000 years ago. The amount of CO₂ emitted from the terrestrial biosphere into the atmosphere is estimated at 320 Pg from pre-historic times up to 1850,⁸ and 136 ± 55 Pg between 1850 and 1998.¹⁰ Until the 1940s, more CO₂ was emitted by land use change than by fossil fuel combustion, and presently about 18% of the total annual emission (1.6 Pg out of 9.1 Pg) in 2008 comes from deforestation, biomass burning and soil cultivation. In comparison, CO₂ emissions by fossil fuel combustion between 1850 and 1998 is estimated at 270 ± 30 Pg C. Such estimates of the historic C loss are important because these statistics provide a reference point with regards to the potential sink capacity of the terrestrial biosphere. Assuming that the estimates by Ruddiman are approximately correct, total C emission from the terrestrial biosphere is about 456 Pg. With 4 Pg of C being equal to 1 ppm of atmospheric CO₂,¹¹ the potential sink capacity of the terrestrial biosphere is about 114 ppm. Further assuming that 40 to 50% of the historic C loss can be resequenced over the next 40 to 50 years (by 2050 to 2060), the strategy of restoring soils and vegetation in world's ecosystems can transfer atmospheric CO₂ by 45 to 55 ppm (average of 50 ppm) into the terrestrial biosphere. Therefore, the strategy of C sequestration in soil and biota is an important option that requires a critical and an

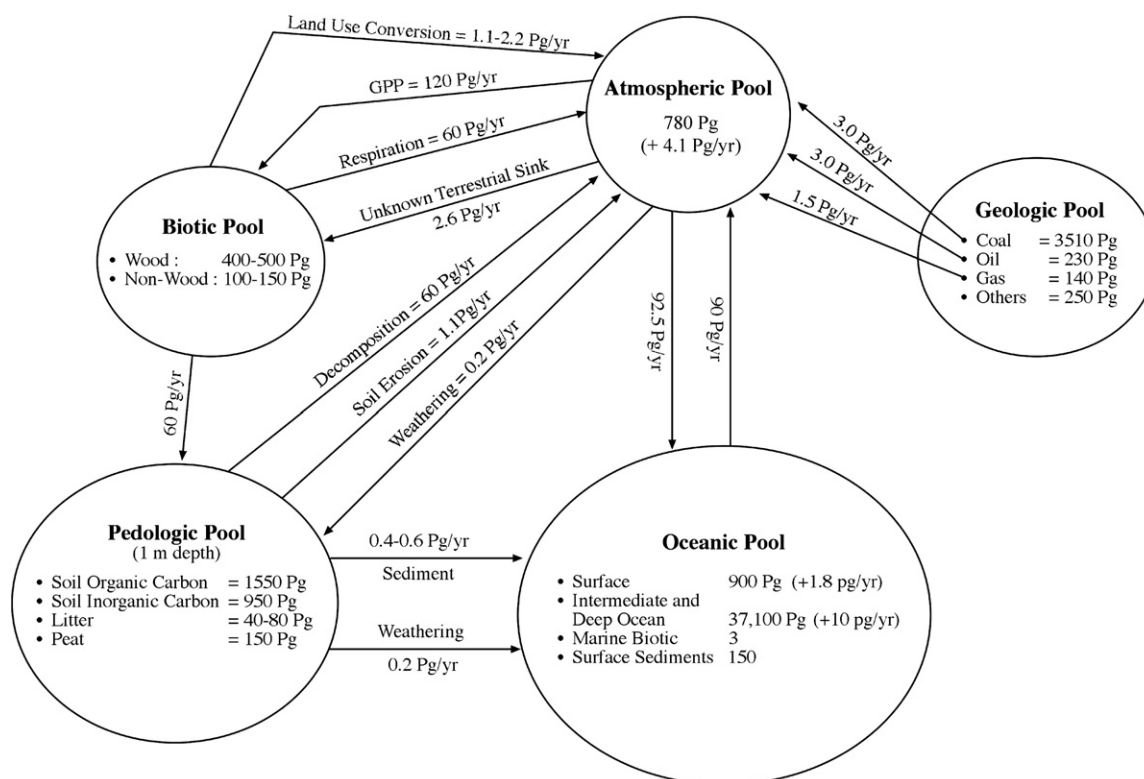


Fig. 1 Estimates of the global pools and fluxes between them.^{1,4,5,7,152}

objective evaluation *vis-à-vis* other technological options of stabilizing the atmospheric CO₂ concentration.

III. Strategies for managing atmospheric CO₂ enrichment

The CO₂ loading of atmosphere can be reduced by biological, chemical, and technological options using two strategies: adaptive options and mitigative options (Fig. 2). Adaptive options are based on adjustments in land use systems within the terrestrial

and aquatic biosphere (*e.g.*, forests, deserts, agriculture, wetlands, coastal ecosystems). Mitigation options involve two approaches: reducing emissions and sequestering emissions. Reducing emission involves using techniques to enhance energy use efficiency, making life style changes, and substituting fossil fuels by low-C or no-C fuel. Sequestering emission involves transfer of atmospheric CO₂ into other pools where it is securely stored and has a minimal chance of leakage back into the atmosphere. There are several options of C sequestration, including geologic, oceanic, chemical, and terrestrial (Fig. 2).¹²

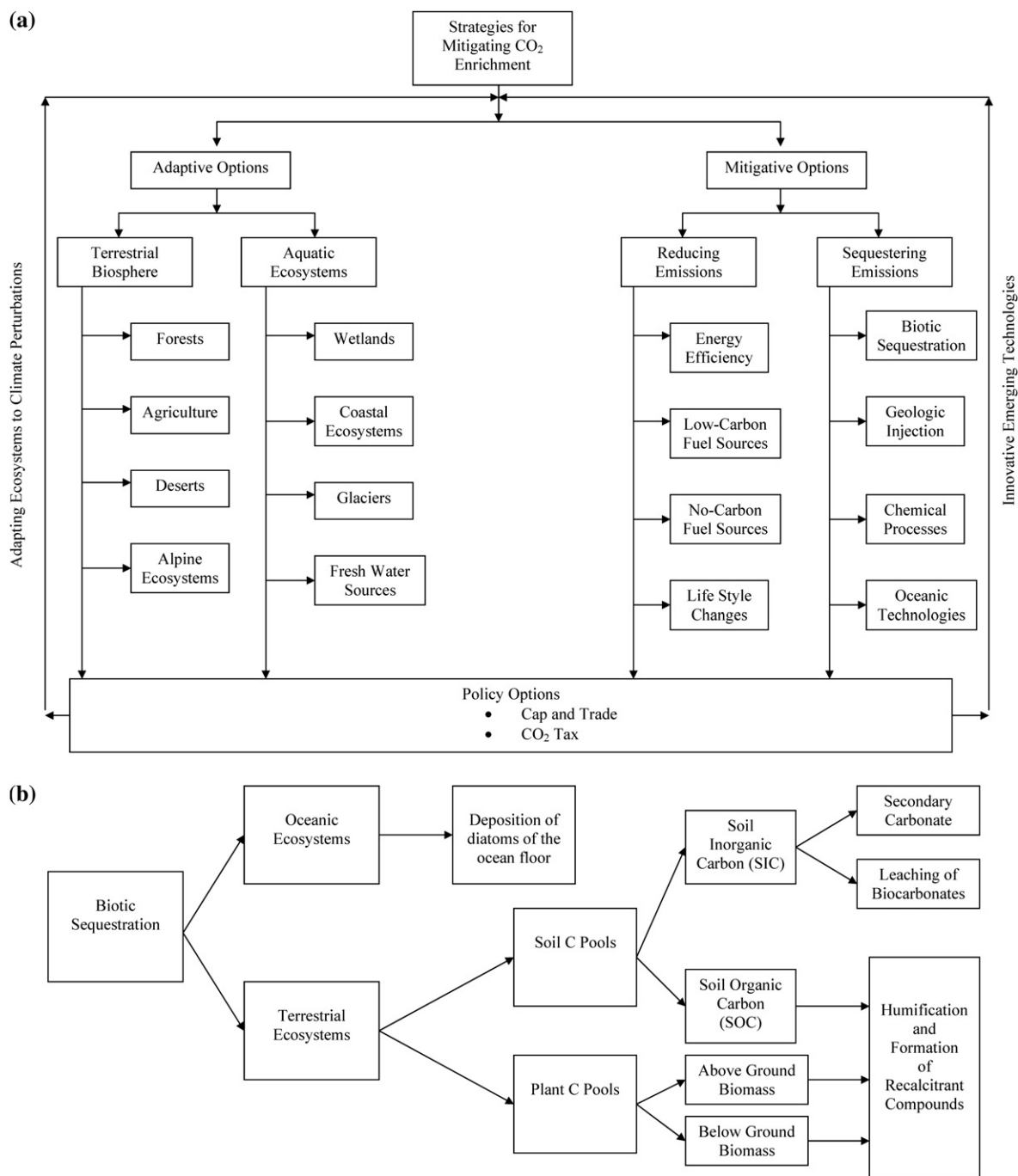


Fig. 2 (a) Technological options for adapting to and mitigating atmospheric abundance of CO₂. (b) Processes of carbon sequestration within the biosphere.

a. Geologic sequestration

Underground storage of industrially emitted GHGs or geologic sequestration involves transfer of atmospheric CO₂ into geologic strata for long-term and secure storage. It comprises capture, purification, liquefaction, transport and injection of CO₂ from a point source into deep (~1000 m) geologic strata or the geosphere. Industrially emitted CO₂ can be injected into several geologic formations including depleted or active oil reservoirs, unmineable coal seams, and saline aquifers.^{13,14} Furthermore, co-injecting CO₂ with H₂S or SO₂ (products of coal gasification and combustion) is also an option to mitigate disposal of these gases.¹⁵ Over time, the trapped CO₂ reacts with minerals and organic substances to form carbonates of Ca, Mg, and Fe *etc.*^{2,16–19} The process has been used since the 1970s to primarily enhance oil recovery (EOR) from old wells.²⁰ Similar to EOR, injection of CO₂ in coal seams displaces coal bed methane (CBM). Because CO₂ is strongly absorbed onto the coal,²¹ unmineable coal seams are a possible option for geologic storage of CO₂.^{22–24} Liquefied CO₂ can also be injected into saline aquifers^{25,26} where it slowly reacts with minerals to form carbonates.

Despite its potential, the geologic sequestration techniques are a work in progress.¹² There remains much to be learned, especially with regards to the rate at which specific geologic formations can accept CO₂ and the impact of injection into the neighboring wells. The cost of drilling and constructing a safe and secure pipeline is another major consideration. Measurement, monitoring and verification (MMV) for any leakage is an important issue that must be addressed. Because of the potentially adverse effects of CO₂ leakage (such as from Lake Nyos in Cameroon in 1986)²⁷ leakage verification is an important consideration for any undertaking of geologic sequestration.²⁸ There is also a strong need to assess degradation of well cement by CO₂ under geologic sequestration conditions.²⁹ Monitoring seismic activity is also important to secure storage of injected CO₂.³⁰ Assessment of injected CO₂ with rock interaction is also important.¹⁷ An integrated decision support system is needed for management of CO₂ in geologic storage.³¹ Therefore, managing the risks of geologic storage is a crucial issue,³² which is subject to regulations by EPA.³³ Despite these limitations, geologic sequestration is an attractive option to energy industry and policy makers because of its potentially large storage capacity.¹²

b. Oceanic sequestration

Similar to the terrestrial C cycle, the marine C cycle also plays a major role in controlling the atmospheric abundance of CO₂. Being the largest pool, ocean is the ultimate reservoir for global C. Oceanic uptake presently accounts for about one-third or 2.5 Pg out of 7.5 Pg of emission from fossil fuel combustion in 2008 (Fig. 1).³⁴ The temperature of the ocean and partial pressure of CO₂ in the atmosphere are important factors. With temperature lag between the ocean and the land and rapid increase in atmospheric abundance of CO₂, the oceanic uptake is expected to increase over time.³⁵ Therefore, oceanic fertilization is one of the strategies for sequestration of atmospheric CO₂.^{36–38} There are two options for CO₂ sequestration in ocean: (i) deep injection of liquefied CO₂, and enhancement of uptake by the marine

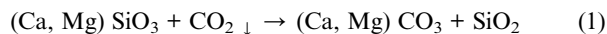
phytoplankton through micronutrient fertilization. Injection of CO₂ under the ocean is one of a wide range of engineering techniques of disposing industrial point-source emission. The density of liquid CO₂ is higher than that of CO₂ for depths below 3000 m.^{39,40} The liquid CO₂ injected creates a pool which eventually seeps into the sediments through gravity-driven displacement of seawater. Several chemical and hydrodynamic processes can occur at the CO₂ (liquid)/saline water interphase including: (i) counter-current diffusion of the two phases, (ii) convective or mass flow driven by ocean currents, (iii) chemical reaction leading to formation of carbonates and bicarbonates, and (iv) salting out.⁴⁰ Porosity and permeability of the sediments are important factors determining the deep penetration of liquid CO₂ into the sediments. It is argued that deep oceanic injection could absorb a large proportion of anthropogenic emissions for many centuries.^{41,42}

The process of oceanic uptake by marine phytoplankton is termed “biological pumping” of C from the upper layers into the deep sea. Reduction in concentration in the upper layers through biotic uptake increases flux from the atmosphere into the ocean. The magnitude of the “biological pumping” is presumably limited by the lack of some micronutrients. The so called “iron hypothesis” is based on the assumption that lower atmospheric CO₂ during glacial times was due to iron fertilization of the surface waters by enhanced dust deposition.^{43,44} In this regard, the Southern Ocean is recognized as the oceanic body most sensitive to climate change.⁴⁵ Application of iron has shown a strong increase in biological production of marine phytoplankton^{46–56,151} Though C is not removed permanently, it is sequestered for up to a thousand years. Phytoplankton bloom, which plays a crucial role in pelagic food webs and “biological pumping”, is also influenced by species composition⁵⁷ and availability of macronutrients such as phosphates (HPO₄) and nitrates (NO₃). Phytoplankton growth is limited by micronutrient (Fe) deficiency on ~25% of the oceanic surface and by macronutrient (NO₃, HPO₄) on ~75% of the oceanic surface.⁵⁸ Fertilizing the ocean with Fe may increase primary productivity in high nitrate low chlorophyll (HNLC) regions such as the Southern Ocean.⁵¹ Besides, some phytoplanktons also produce dimethyl sulfide which acts as a cloud condensing nucleus. Increase in cloud cover increases albedo and lowers temperature.⁵⁹ The seemingly vast potential of ocean fertilization on enhancing the “biological pumping” is constrained by several adverse environmental impacts^{12,60} and uncertainties,⁶¹ which must be objectively addressed.

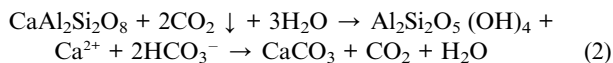
c. Chemical weathering and CO₂ sequestration

Chemical weathering of rocks and minerals at the continental scale is a geological process that moderates atmospheric concentration of CO₂ on a geological time scale.^{62,63} A fraction of biomass-derived CO₂ in the soil is diverted to the soil inorganic carbon (SIC) pool through weathering of Ca/Mg-bearing silicates, and of carbonates (*e.g.*, limestone). The weathering of silicate minerals moderates atmospheric CO₂ concentration on the millennial time scale, and that of carbonates on the centennial scale.^{64–66} Furthermore, rates of carbonate mineral weathering are orders of magnitude faster than those of silicate weathering.⁶⁷

(i) **Weathering of silicates.** Precipitation and temperature are important factors affecting weathering of silicate minerals. The slow process of geological weathering converts Ca/Mg bearing silicates into carbonates with dissolution of silica eqn (1).^{68,69}



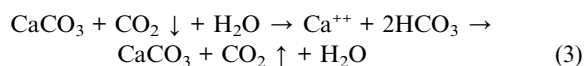
The downward arrow indicates uptake or sequestration of atmospheric CO₂. Predominant minerals involved in this reaction are plagioclase, olivine, pyroxene, and volcanic glass. These minerals are weathered into aluminosilicates or clay minerals (e.g., kaolinite, halloysite, imogolite, allophane). A specific reaction is as follows:⁷⁰



Transport of Mg²⁺, Ca²⁺ and HCO₃⁻ from the weathering site leads to net removal of CO₂ from the atmosphere.

In contrast with weathering of Ca/Mg silicates, weathering of Na–K silicates (feldspars, white mica) into clays (e.g., kaolinite) does not cause net removal of atmospheric CO₂.⁷⁰

(ii) **Weathering of carbonates.** Similar to weathering of feldspars and white mica, weathering of limestone (CaCO₃) and its reprecipitation in the ocean is also a CO₂ neutral reaction (eqn (3)). The reaction depicted in eqn (3) shows that 1 mole of CO₂ absorbed during the weathering is re-emitted into the atmosphere upon its precipitation. The process merely transfers carbonates from the land into the ocean.

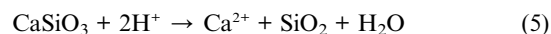
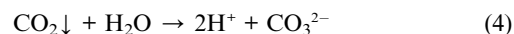


The upward arrow indicates emission of CO₂ back into the atmosphere. Thus, weathering of limestone is a CO₂ neutral process.⁷⁰

(iii) **Leaching of bicarbonates.** Dissolution of biomass-derived CO₂ in soil, reaction of carbonic acid thus formed with carbonate minerals in soil, and leaching of bicarbonates into aquifers or eventual transport to the ocean is an important process of taking CO₂ out of the atmosphere. Leaching of HCO₃⁻ is especially pertinent in systems of partial or complete soil leaching with a good quality water. The process is also relevant to ~300 Mha of world's irrigated cropland whenever groundwaters unsaturated with Ca(HCO₃)₂ are used for irrigation. The rate of leaching may be 0.25 to 1.0 Mg C ha⁻¹ y⁻¹,⁷¹ with a total potential of 75 to 300 Tg C y⁻¹.

(iv) **Mineral CO₂ sequestration through industrial processes.** The natural principle of mineral CO₂ sequestration by weathering of silicates can be mimicked in an industrial setting in which Ca²⁺ and Mg²⁺ containing minerals are converted into carbonates in a catalysed controlled process (eqn (1)). However, the natural process is too slow and must be accelerated under controlled environments.⁷² The process has numerous advantages:⁷³ (i) the product is thermodynamically stable and, (ii) cost and energy consumption are low because the reaction is

exothermic (CaO + CO₂ = CaCO₃ + 179 kJ mol⁻¹, MgO + CO₂ → MgCO₃ + 118 kJ mol⁻¹). A major disadvantage is that large amounts of Ca²⁺ and Mg²⁺ minerals are required to sequester a significant amount of CO₂. The amount of minerals required to bind CO₂ produced by 1 Mg of C is 4.7 Mg of CaO and 3.4 Mg of MgO.⁶⁹ A large amount is needed for rocks containing a small fraction of these minerals. Accelerating the natural process to make it industrially viable requires several routes including the aqueous carbonate route.⁷⁴ The chemical reaction described by Huijgen *et al.*⁷³ are shown in eqn (4) to (6).



These reactions are accentuated either through energy-consuming pre-treatment or high Ca²⁺ concentration.

IV. Utilization and recycling of CO₂

Rather than treating it as a waste (garbage) to be disposed of in underground or undersea reservoirs, industrially emitted CO₂ is an important resource with numerous applications. Indeed, with increasing world population and dwindling supplies, industrially emitted CO₂ must be recycled and used as a raw material for a range of chemical and biological products including enhancing agronomic/food production. For production of chemicals, CO₂ can be used as a source of C, co-reagent or a solvent in a wide range of industrial processes, ref. 2,75,76 outline several chemical reactions for using CO₂ as a source of carbon in a variety of synthetic processes. Using CO₂ to produce biomass and create bioeconomy, based on enhanced production in both terrestrial and marine ecosystems, has a vast economic potential awaiting to be realized (Fig. 3). In addition to the CO₂ fertilization effect and improving agronomic and forestry production, biomass produced through growth of macro- and micro-algae and cyanobacteria using bioreactors has major applications in biofuels, biochemicals, and biochar (Fig. 4). One kg of biofuel is obtained from 5–10 kg of biomass.⁷⁷ An important variant of this process is C sequestration in terrestrial ecosystems both as forest

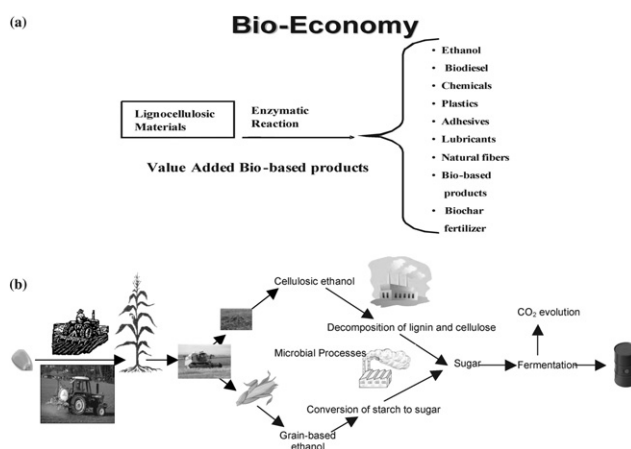


Fig. 3 The bioeconomy based on biomass.

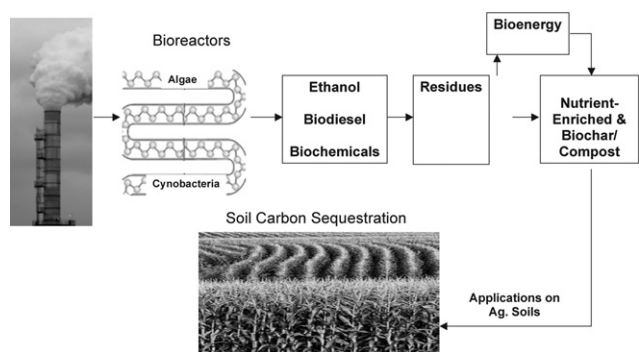


Fig. 4 Using industrial carbon dioxide in bioreactors to produce biofuel, biochar for use as soil amendment, and other bioproducts.

biomass and SOM in agroecosystems. The latter, with significant implications to soil quality, water quality and global food security, is described in the following sections.

Chemical and engineering barriers to lignocellulosic biofuels are being broken through scientific advances.⁷⁸ To be economic, production of biofuels must be linked with that of biomaterials. The strategy is to fully integrate the agro–biofuel–biomaterial–biopower cycle.⁷⁹ Such an integration requires a well planned road map for the biorefineries, chemical processing industries, and farming systems of the 21st century.

V. Soil organic matter in agroecosystems

The importance of organic matter (OM) or more appropriately the SOM to soil quality, its capacity to produce economic goods and perform ecosystem services, has been recognized for millennia. The humus, highly reactive and decomposed component of SOM, impacts soil's physical, chemical and biological properties, and imparts the characteristic dark brown color which is synonymous with the soil of a good quality. Allison⁸⁰ stated that “soil organic matter has, since the dawn of history, been the key to soil fertility. For 8000 years or more, man has appreciated the fact that dark soils are usually productive soils”. Homer (Greek Poet 900–700 BC) emphasized regular manuring of vineyards, probably because its application enhanced SOM concentration and improved productivity. Xenophon (434–335 BC) stated that “the estate has gone to ruins because someone didn't know it was well to manure the land”.⁸¹ Similar to the European farming, the significance of manuring to enhancing soil quality has long been a cultural tradition in Asia. King^{82,83} stated that “China, Japan, Korea and other countries of eastern Asia have a long tradition of recycling OM to enhance soil fertility”. It was partly because of manuring that the settled agriculture in these densely populated countries has been practiced for 3 to 5 millennia. Similar to East Asia, manuring also has been used since antiquity in the Mediterranean region,⁸⁴ in the Middle East since prior to the biblical era,^{85,86} and since ~1500 BC in South Asia (SA) region by the Harappan civilization in the Indus Valley. Two books written about 300 BC “Arthashastra” by Kautilya and “Krishi” vividly describe the benefits of using animal manure to improving soil fertility.⁸⁷

The use of manuring continued at the onset of the Christian era. Feller⁸⁸ described the historical developments with regard to

the importance of SOM. He observed that the Roman philosopher Virgil⁸⁹ (1 AD) implied “humus” as soil, and used the words “humus”, “solum” and “terra” interchangeably. Ibn-Al-Awan, a 12th century Moorish philosopher, wrote in the book “Kitab-Al-Filaha” (Book of Agriculture) that “the first step in the science of agriculture is the recognition of soils and of how to distinguish that which is of good quality and that which is of inferior quality. He who does not possess this knowledge lacks the first principles and deserves to be regarded as ignorant”. He further stated that “one must also take into consideration the depth of the soil, for it often happens that its surface layer may be black”.⁹⁰ The emphasis on the black color of the surface layer signifies the importance that he gave to the beneficial effect of humus on soil quality, because in general soils of darker color have high SOC content and are of better physical, chemical and biological quality.

The recognition of the importance of humus to soil quality increased with the development of modern farming in the early 19th century. In the book “Principles of Rational Agriculture” (published in German in 1809 and translated in French and English in 1811), Thaër⁹¹ defined that humus “is the residue of animal and vegetable putrefaction. It is a black substance”.⁸⁸ Muller⁹² described different types of horizons containing humus as mull (mould) and torf (peat).

The knowledge of soil science, as a distinct discipline, increased progressively during the first half and drastically during the second half of the 20th century. Waksman⁹³ stated that “The importance of humus in human economy seldom receives sufficient emphasis. Suffice to say that it probably represents the most important source of human wealth on this planet. Nature has stored in and upon the earth, in the form of humus, the source of a vast amount of readily available energy, a large part of carbon needed for life processes, and most of the combined nitrogen, so much needed for plant growth”. In the USDA's Year Book of Agriculture “Soil and Men”, Albrecht⁹⁴ stated the importance of SOM to soil's quality. He wrote that “the high productivity of most virgin soils has always been associated with the high content of SOM, and the decrease in supply with cultivation has generally been paralleled by a corresponding decrease in productivity.” Albrecht also narrated that “Soil organic matter is one of our most important national resources; its unwise exploitation has been devastating, and it must be given its proper rank in any conservation policy as one of the major factors affecting the levels of crop production in the future.” Sir Albert Howard⁹⁵ stated that “In a fertile soil, the soil and plant come into gear in two ways simultaneously. In establishing and maintaining these contacts, humus is essential. It is, therefore, a key material in the life cycle. Without this substance, the wheel of life cannot function effectively.” Sir Albert Howard⁹⁶ further stated that “humus is the most significant of all Nature's reserves.”

The importance of SOM as a moderator of the global climate began in the later part of the 20th century. Jenny⁹⁷ stated that contributions of SOM to atmospheric CO₂ appear underestimated. Since then, the literature is replete with the data on the importance of enhancing SOM and sequestering C in soil and terrestrial ecosystems to mitigate the climate change by offsetting fossil fuel emissions.^{98–102} It is also hypothesized that emission of CO₂ from soil into the atmosphere began with the onset of settled agriculture, and that of CH₄ with cultivation of

Table 1 Direct and ancillary benefits and ecosystem services provided by the soil organic matter pool

Direct benefits	Ancillary benefits and ecosystem services
1. Improves soil structure and tilth	1. Sequesters atmospheric CO ₂
2. Reduces soil erosion	2. Enhances soil's ability to oxidize CH ₄
3. Decreases non-point source pollution	3. Restores degraded ecosystems
4. Purifies water	4. Increases soil/terrestrial biodiversity
5. Denatures pollutants	5. Enhances use efficiency of input (water use efficiency, nutrient use efficiency)
6. Increases plant available water	6. Improve wildlife habitat
7. Stores plant nutrients	7. Decreases nutrient and water loss from the ecosystem
8. Improves crop/biomass yield	8. Enhances ecosystem resilience
9. Provides food/energy for soil biota	9. Strengthens recycling mechanisms
10. Buffers impact of perturbation on soil properties	10. Improves the environment

Table 2 Soil organic matter and climate change

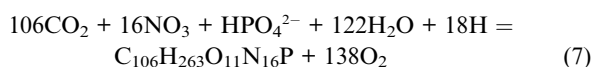
Will climate change:	Will soil processes:
(1) Amplify SOM depletion	(1) Have mitigative impact
(2) Exacerbate soil erosion	(2) Adversely impact agronomic yield
(3) Alter global C cycle more drastically	(3) Increase the land-based C sink
(4) Affect NPP through CO ₂ fertilization effect	(4) Decrease SOC pool through C-input in soil at high temperatures

rice paddies and domestication of animals.^{8,9} With 1 Pg of soil C being equivalent to 0.47 ppm of atmospheric CO₂, emissions from world soils could have contributed 37 ppm of the total increase of 105 ppm or 35% of the cumulative gain in the atmospheric abundance from 280 ppm in ~1750, to 385 ppm in 2008. For each 4 Pg of fossil C burned, the atmospheric abundance of CO₂ increases by 1 ppm.¹¹

The biotic sequestration of CO₂ through photosynthesis is a natural process. It involves natural and managed interventions for retaining a small fraction of approximately 120 Pg of CO₂-C annually photosynthesized by terrestrial and aquatic biospheres. Being a natural process, it is cost effective, has numerous ancillary benefits, and little or none environmental/health risks (Table 1). Despite its positive impact on numerous ecosystem services, there are several uncertainties in the SOM pool with regards to the projected climate change (Table 2). Understanding basic processes governing biogeochemical cycling of C is essential to minimize these uncertainties.

VI. Carbon sequestration in terrestrial ecosystems

The strategy of C sequestration in terrestrial ecosystems is based on the natural photosynthetic process of transferring atmospheric CO₂ into the biomass (eqn (7)),⁷⁰



Most of the 120 Pg of C photosynthesized annually is balanced either by direct plant respiration or by microbial decomposition. However, even if 6 to 7% of 120 Pg photosynthesized annually can be retained in the biosphere, it can effectively off-set anthropogenic emissions due to fossil fuel combustion and cement manufacturing estimated at 7.5 Pg y⁻¹,⁵ and 1.6 Pg y⁻¹ by deforestation and land use conversion⁶ (Fig. 1). Choosing a judicious land use and adopting recommended soil/plant management can enhance retention of some photosynthetic C in the terrestrial/marine biosphere (Fig. 5). The processes can be enhanced through managing coupled cycles of C, N and H₂O which would positively influence soil quality, environment quality and the biomass productivity. Managing terrestrial C sequestration would also advance food security because of increase in use efficiency of agricultural input. There is a wide range of agricultural production systems for enhancing energy use efficiency. Important among these are (Fig. 6): (i) no-till or conservation tillage systems with mulching and cover cropping for seedbed preparation and weed control, (ii) integrated nutrient management (INM) along with biochar and slow release formations for soil fertility management, (iii) water harvesting and recycling with drip/furrow irrigation, and (iv) use of improved germplasm tolerant to biotic and abiotic stresses (Fig. 6). Some studies have shown that Bt (*Bacillus thuringiensis*) plant residues have a high lignin content¹⁰³⁻¹⁰⁵ and thus more resistant to decomposition than non-Bt residues.^{106,107}

Strategies for C sequestration in terrestrial ecosystems are outlined in Fig. 7. The goal is to: (i) enhance production per unit area, time and input on existing farmland through agricultural intensification, (ii) control soil erosion and restore degraded soils, (iii) undertake afforestation and reforestation of degraded and marginal soils, (iv) establish biofuel plantations, and (iv) use biochars as a soil amendment (Fig. 7). The objective is to enhance ecosystem services in terms of water quality, nutrient cycling, biodiversity, increase in NPP, and off-setting emissions.

Soil and crop management practices which enhance the input of biomass-C into the soil (e.g., no-till farming, and using fertilizer, manure, irrigation, mulch) normally increase the ecosystems C pool:^{10,101} although net gains in C pool depend also on the hidden C costs of the techniques used.¹⁰⁸ Some of the management practices which require special mention are briefly describe below:

(a) Agricultural liming

Use of lime on acid soils may affect weathering of silicates and export of bicarbonates. Oh and Raymond¹⁰⁹ observed that net atmospheric C sequestration by liming through transport of bicarbonates in streams in the Ohio River Basin was 9.5 kg C ha⁻¹ y⁻¹. However, the effect of liming on biomass production, SOC dynamics or the emission of CO₂ reaction in acidic soil was not assessed. Further, the net effect of liming on soil C pool depends on soil-specific factors. In Scotland, Rangel-Castro *et al.*^{110,111} observed that more soil C was lost than gained through photosynthesis because of pasture liming from 1990 to 1998. These researchers observed that turnover of the recently

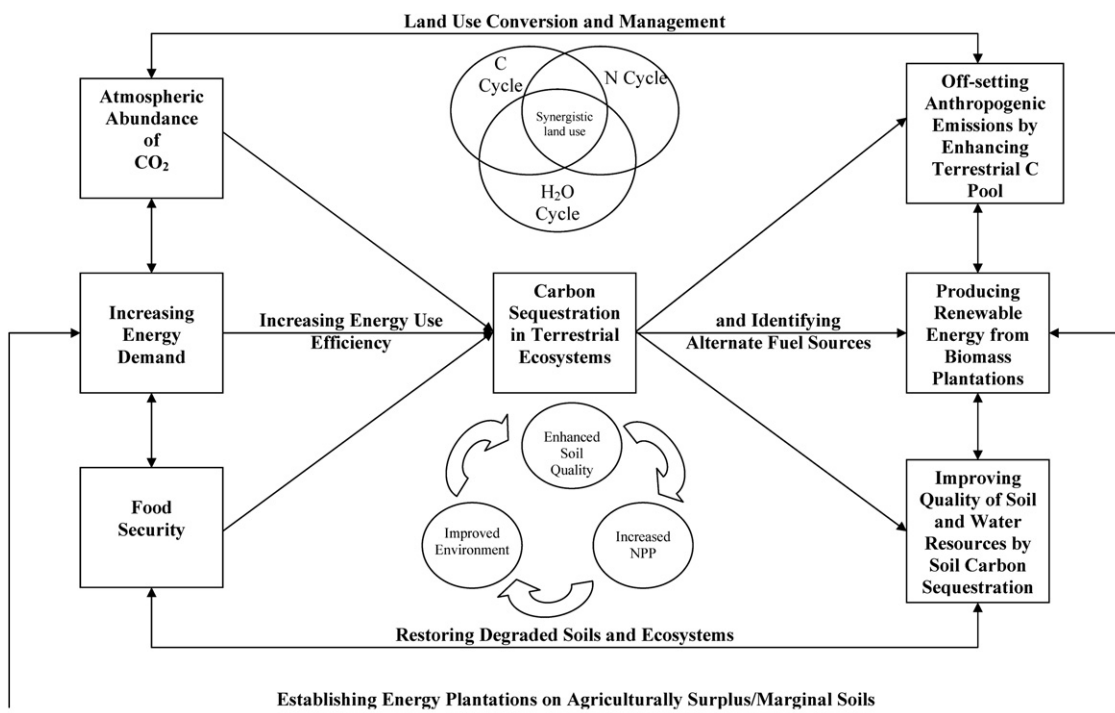


Fig. 5 Addressing global issues of atmospheric enrichment of CO₂, increasing energy demand and exacerbating food insecurity through carbon sequestration in terrestrial ecosystems.

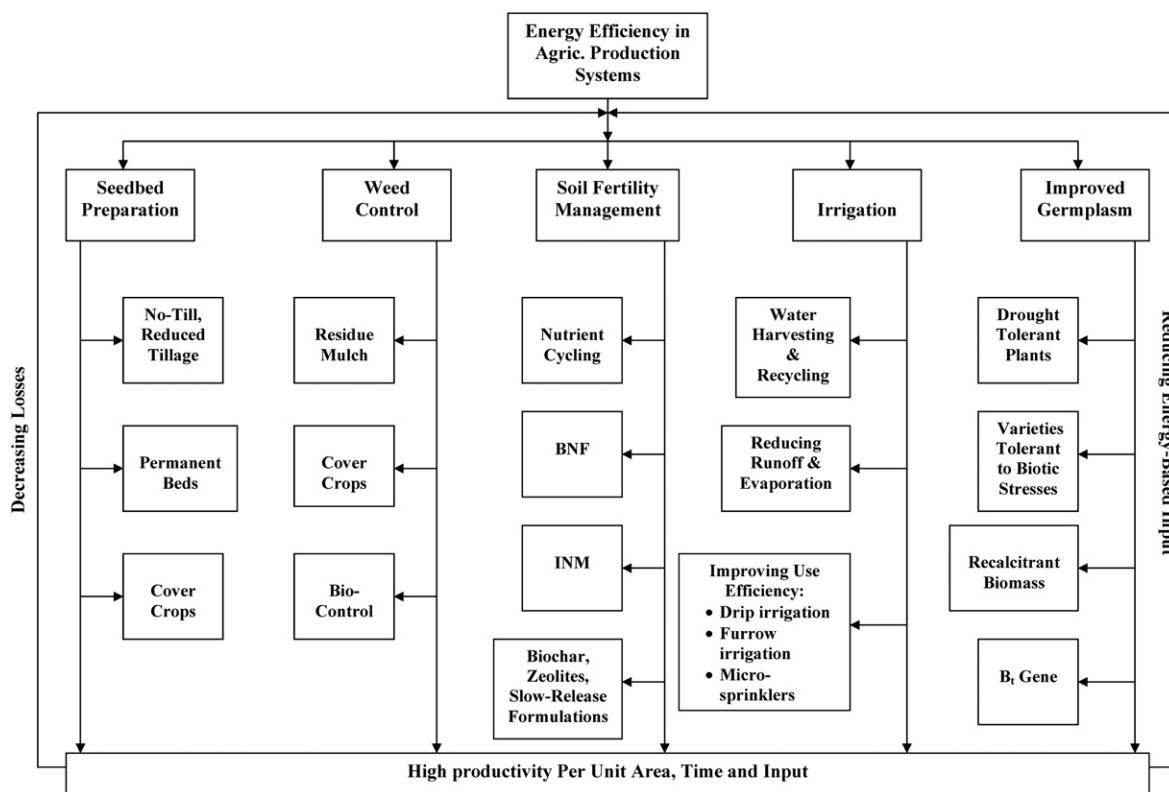


Fig. 6 Increasing energy use efficiency in the agricultural production system.

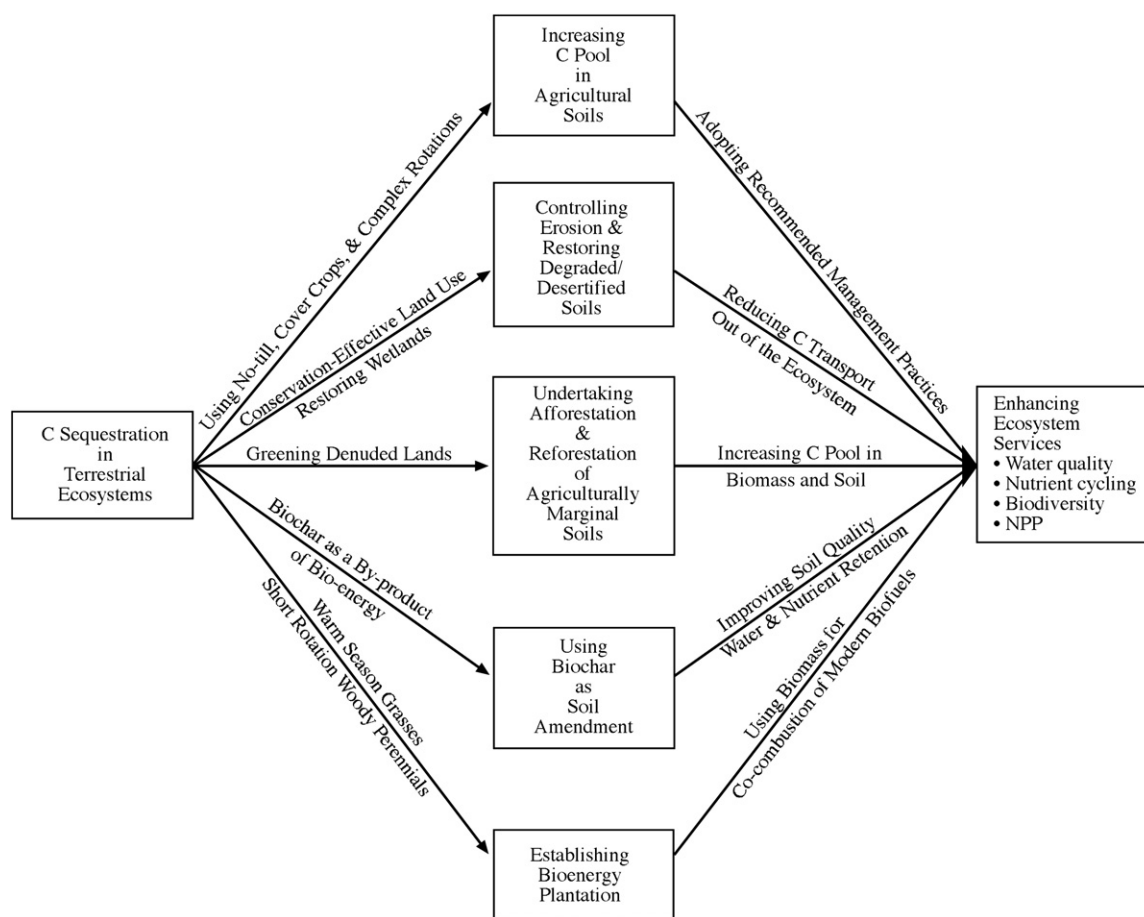


Fig. 7 Strategies for carbon sequestration in terrestrial ecosystems.

assimilated ^{13}C compounds was faster in microbial biomass from limed than that from unlimed soil, suggesting that liming increases incorporation by microbial communities of root exudates.

(b) Nitrogen management

The nitrogen cycle strongly interacts with the C cycle, and N is needed in creation of biomass C into stable soil humus. Further, N availability may also increase the photosynthetic reaction (eqn (7)) in N-limited soils both in agricultural and forest ecosystems. Indeed, the CO_2 fertilization effect may also be limited by the lack of adequate N.^{112,113} The impact of N fertilizer on biomass production is likely to increase in developing countries such as Africa, where the rate of fertilizer use is at present only $5 \text{ kg ha}^{-1} \text{ y}^{-1}$ compared with $\sim 200 \text{ kg ha}^{-1} \text{ y}^{-1}$ in developed countries. In addition to N, soils of the tropics are also deficient in P and cations (Ca^{2+} , Mg^{+}). Unless, other nutrients are available, increase in application of N may accentuate losses by volatilization (N_2O) and leaching (NO_3), and depletion of the SOC pool.^{114,115} The Haber-Bosch process of producing reactive N as a mineral fertilizer has saved billions from starvation,¹¹⁶ and lack of its application in Africa and elsewhere is the cause of perpetual food insecurity, hunger and malnutrition.

While judicious use of reactive N as a fertilizer in agroecosystems is essential, its impact on SOC dynamics remains to be a controversial topic,¹¹⁷ and needs to be critically and

objectively assessed. This debate must be resolved on the basis of systematic, well designed and long-term field experiments, because the effect of N may depend on other management parameters. For example, Russell *et al.*¹¹⁸ assessed the impact of N fertilization rate and cropping systems on C pool in soils of Iowa. Grain and biomass yields increased with increase in N input. The SOC concentrations were significantly higher only in systems containing alfalfa in the rotation cycle. In China, Zhu *et al.*¹¹⁹ reported that it was the application of farm yard manure for 25 years rather than N fertilizer that increased SOC concentration. In Canada, Malhi *et al.*¹²⁰ observed that total SOC was generally more with than without straw retention for all levels of N application. A long-term study in Illinois, USA, showed that the SOC pool increased with an increase in the rate of N application.¹²¹ Sainju *et al.*¹²² reported that the SOC concentration in 0–30 cm depth increased when cover crops (hairy vetch, *Vicia villosa* Roth; rye; *Secale cereale* L) were included in the rotation and N fertilizer was applied at the rate of 120 to 130 $\text{kg N ha}^{-1} \text{ y}^{-1}$. In Brazil, Diekow *et al.*¹²³ observed that the average SOC sequestration rate of legume-based cropping systems was $1.42 \text{ Mg C ha}^{-1} \text{ y}^{-1}$ with N application. These studies show that effectiveness of N application for SOC sequestration depends on residue retention as mulch, inclusion of cover crops in the rotation cycle and adoption of complex crop rotations, and use of INM practices such as application of compost, farm yard manure and biochar.

(c) Biochar

Another mechanism of enhancing the SOC pool is through application of black C or biochar extracted from controlled combustion of biomass. The biochar C applied to soil has a long residence time. Using biochar is mimicry of the natural process in which some biomass from forest and grassland fires is not fully burnt but is “carbonized” and added to the soil as a relatively recalcitrant charcoal or biochar.¹²⁴ Using this principle, there are some man-made soils with high concentration of C. These soils in the Amazon are called “Terra Preta do Indio” (Indian Black Earth).^{125,126} Ever since the discovery of “Terra Preta do Indio”, large pockets of permanently fertile soils in otherwise highly leached and acid soils of the Amazon region, there is a growing interest in using biochar as a soil amendment.^{127–129} The application of biochar to soil as an amendment is considered an option to off-set emissions while improving soil quality—a new green¹³⁰ or a charcoal vision.¹³¹ Consequently, pyrolysis plants are being established^{132,133} to commercialize the production of nutrient fortified biochar as a soil amendment. While some consider black C sequestration as an alternative to bioenergy,¹³⁴ others have reported an increase in losses of forest-derived humus and loss of native soil C due to application of biochar.¹³⁵ Similar to biofuel, there is also a strong need for complete life cycle analysis of the biochar production system, application, and fate of charcoal vs. native C in soil humus.

VII. Biofuels and the carbon cycle

Increase in the energy cost and threat of global warming because of the atmospheric enrichment of CO₂ have increased emphasis on biofuel production. Production of biofuels affect the global C cycle directly and indirectly. Directly, biofuels avoid emissions of CO₂ by merely recycling it. Indirectly, production of biofuels can accentuate CO₂ emissions by using reactive nitrogenous fertilizers and other energy-based input in production of corn grains and soybeans (USA), and sugarcane (Brazil). These 3 crops require the use of N-fertilizers (soybeans require less N than corn and sugarcane) which normally has low use efficiency of ~30%. Thus, N-intensive biofuels could negate any savings in C emission.¹¹⁴ Removal of crop residues for ethanol production can degrade soils by accelerated erosion and exacerbate emission of CO₂. Conversion of natural to agricultural ecosystems can enhance gaseous emissions from land use change.¹³⁶ Deforestation of tropical rain forest for additional land can exacerbate CO₂ emission.¹³⁷

The biomass production potential of energy crops ranges from 10 to 22 Mg ha⁻¹ y⁻¹ for short rotation woody crops in the U.S. and 20 Mg ha⁻¹ y⁻¹ in Brazil with a global average of about 10 Mg ha⁻¹ y⁻¹.⁷⁹ The biomass productivity of energy plantations can be increased by identifying biotic and abiotic constraints of species to be grown in an ecoregion and addressing those constraints through site-specific research including: (i) tolerance to drought, cold and heat, (ii) resistance to pests and diseases, (iii) addressing dormancy, floral sterility and delayed leaf senescence, (iv) more carbon allocation to stem diameter vs. height growth, (v) more shoot : root ratio to optimize the aboveground (stem) biomass, (vi) high H₂O, N and nutrient use efficiency, (vii) high biomass production per unit area and time, (viii) readily

processable cellulose, hemicellulose and lignin in the biomass, (ix) desired biomass composition, and (x) potential to produce value added chemicals.⁷⁹

Despite the high biomass production strategy, the competition for natural resources (land area, water, nutrients needed for food production) is a concern that is likely to exacerbate with an increasing world population. Two issues that need an objective and critical appraisal with regards to biofuels are:¹³⁸ (i) the magnitude of emissions avoided from use of biofuels, and (ii) the impact of alternative land use strategies on C sequestration in the biosphere. Production of biofuels is a viable option if the net amount of emission avoided exceeds the quantity of C sequestered in the terrestrial biosphere. The net amount of emission avoided includes the C equivalent of energy required to produce biofuel (*e.g.*, fertilizer, pesticides, processing). The data in Table 3 by Righelato and Spracklen¹³⁸ show that afforestation of an equivalent area would sequester 2 to 9 times more C over a 30 year period than the emissions avoided by the use of biofuels. It is estimated that 10% substitution of petrol by biofuels would require additional 43% of the current cropland area in the U.S. and 38% in Europe.¹³⁹ Deforestation and biomass burning of the tropical rainforest lead to a large up-front emission. Of all the options, conversion of woody biomass to ethanol may be compatible with afforestation because many biofuels have greater aggregate environmental costs than petroleum.

Detailed life cycle analysis is needed to assess the net C loss or gain upon conversion of native ecosystems to biofuel plantations. Fargione *et al.*¹⁴⁰ computed ecosystem C debt and the number of years required to pay it for conversion of different native ecosystems to biofuel plantations in Brazil, Indonesia, Malaysia and the USA. Because converting native ecosystems to agricultural/biofuel plantations leads to substantial emissions of CO₂ through deforestation/biomass burning and microbial decomposition, the initial loss is termed “C debt” of land use conversion. This debt is to be repaid over time through production of biofuels. The longer the duration to pay the debt, the more long lasting is the adverse impact. The data in Table 4 show that the only viable option is the biofuels from perennials

Table 3 Estimates of emissions avoided by biofuel production *versus* C sequestration by alternative land use strategies over 30 years (recalculated from ref. 138)

Strategy	Process	Emissions avoided/Mg C ha ⁻¹
I. Biofuel	(i) Sugarcane to ethanol	50
	(ii) Wheat to ethanol	15
	(iii) Sugar beet to ethanol	30
	(iv) Maize to ethanol	15
	(v) Rapeseed to diesel	12
	(vi) Woody biomass to diesel	55
II. C sequestration in terrestrial ecosystems	(i) Tropical forest to cropland	-182.5 (emissions)
	(ii) Tropical cropland to forest	160
	(iii) Temperate cropland	-90 (emissions)
	(iv) Temperate cropland to grassland	25

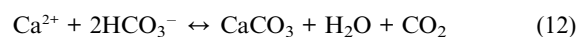
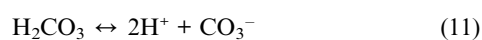
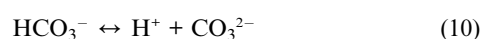
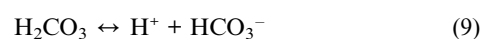
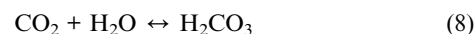
Table 4 Carbon debt upon conversion of native ecosystems to biofuel plantations (adapted from ref. 140)

Former ecosystem	Biofuel	C Debt/Mg C ha ⁻¹			Debt allocated to ethanol (%)	Annual payment/Mg C ha ⁻¹ y ⁻¹	Time to repay debt/y
		Soil	Biomass	Total			
Tropical rainforest	Palm biodiesel	55	135	190	87	1.9	86
Peatland rainforest	Palm biodiesel	218	135	353	87	1.9	423
Tropical rainforest	Soybean biodiesel	65	135	200	39	0.25	319
Cerrado wooded	Sugarcane ethanol	31	14	45	100	2.7	17
Cerrado woodland	Soybean biodiesel	22	1	23	39	0.25	37
Central grassland	Corn ethanol	34	3	37	83	0.33	93
Abandoned cropland	Corn ethanol	18	1	19	83	0.33	48
Abandoned cropland	Corn ethanol	2	—	2	100	1.2	1
Abandoned cropland	Prairie Biomass ethanol	0	0	0	100	2.1	No debt

grown on degraded or marginal croplands. In contrast, biofuels produced from converting rainforests, peatlands, savannas or grasslands emit 17 to 420 times more CO₂ than the GHG emission over 30 years and increase over 167 years. Therefore, a critical appraisal through detailed life cycle analysis and, of food for hungry stomachs vs. tanks, are essential prior to undertaking large scale biofuel production.

VIII. Secondary carbonates

The total soil C pool comprises two distinct components: SOC and SIC. The SIC pool consists of primary or lithogenic carbonates and secondary or pedogenic carbonates. Most soils of arid and semi-arid regions contain primary carbonates such as calcite (CaCO₃), dolomite (CaMg(CO₃)₂), aragonite (polymorph of natural CaCO₃) and siderite (FeCO₃). Primary carbonates are derived from the weathering of soil parent material. In contrast, secondary carbonates are derived from the decomposition of Ca-bearing materials and precipitation of weathering products. Secondary carbonates occur in soils in different forms including precipitates in the interstitial spaces of parent material, prelaminate layers of carbonates, coating on the underside of stones, and as needles or crystals.¹⁴¹ Ryskov *et al.*¹⁴² described several mechanisms of formation of secondary carbonates since the second half of the Holocene in steppe soils of Russia. They divided the process into 3 stages: (i) accumulation of carbonates in the upper 2 m sequence resulting from a high groundwater level 5000–3800 years ago, (ii) redistribution of carbonates in the profile, with removal from the upper horizon and formation of an accumulation horizon 3800–2000 years ago, and (iii) stabilization of the carbonate profile. The slow process of chemical transformation shows that during dissolution, every CaCO₃ molecule binds one CO₂ molecule, which transforms it into biocarbonate. During crystallization, CO₂ is re-emitted back into the atmosphere as carbonates are deposited. Secondary carbonates are formed as a result of precipitation that occurs when super-saturated solution is subject to evaporation, freezing, decline in partial pressure of CO₂, and soil dehydration through transformation. Living organisms (microorganisms, termites, earthworms, some mushroom species, and mollusks) can also facilitate formation of secondary carbonates with dissolution of CO₂ from soil air and uptake of Ca²⁺ and H₂O from soil solution (eqn (8)–(12)).¹⁴³



Secondary carbonate accumulation commonly occurs in pH range of 7.3 to 8.5, and sufficient amount of Ca²⁺ must be present.

There are four general models of pedogenic carbonate formation¹⁴⁴

(i) The *per descendum* model: precipitation of carbonates in the sub-soil following dissolution of pre-existing carbonates in the upper layers and their vertical translocation to sub-soil,

(ii) The *per ascensum* model: secondary carbonates are deposited from capillary rise of Ca²⁺ from shallow water tables,

(iii) The *in situ* model: reprecipitation of carbonates occurs close to bedrock following short-range dissolution, and

(iv) The biogenic model: biological factors (*e.g.*, termites, microbes, and plants) accentuate the precipitation of secondary carbonates.

Measured rates of soil C sequestration through formation of secondary carbonates are low and range from 1.2 to 6 Kg C ha⁻¹ y⁻¹ in southwest USA¹⁴⁵ to 12 to 17 kg ha⁻¹ y⁻¹ in Canada.¹⁴³ With a large area of about 4 billion ha in arid and semi-arid regions, total amount of C sequestration as secondary carbonates at 5 to 10 kg C ha⁻¹ y⁻¹ can be 20 to 40 Tg C y⁻¹. There have also been some concerns whether exposure of caliche to the surface may lead to its weathering and emission of CO₂. Experiments conducted in Southwestern U.S. by Serna-Pérez *et al.*¹⁴⁶ showed that exposed petrocalcic horizons are not actively emitting CO₂.

IX. Carbon sequestration and global food security

In addition to the threat of global warming, C sequestration also impacts global food security. There are presently about 1 billion food-insecure people in the world. The population prone to food insecurity is increasing with the increase in the price of food grains, notably corn, wheat, rice and soybeans. The increase in

food price, adversely affecting the poor population (<\$2 day⁻¹), are due to several complex and interacting factors. Over and above the effects of increase in price of energy (\$135 per barrel of oil in May 2008), perpetuation of drought, in Australia and Ukraine among others, presumably caused by global warming, has adversely affected production of rice, wheat and other food staples. Soil degradation, coupled with high temperatures in early spring, also supposedly caused by global warming, is one of the causes of stagnating or declining productivity of the rice–wheat system in the Indo-Gangetic Basin. Soil degradation, especially by depletion of SOM and the negative nutrient budget on a continental scale, are causes of agrarian stagnation in Sub-Saharan Africa. Climate change may exacerbate the problem of low agricultural production in the West African Sahel.^{147–149} The benefits of improved germplasm cannot be realized unless grown under optimal soil and agronomic conditions because even the improved varieties cannot extract water and nutrients from impoverished soils. The problem of food insecurity for the world's poor is to some extent also affected by the emphasis on biofuels (see section VII). Production of corn grain based ethanol and soybean derived biodiesel affects food security directly by increasing the price of food grains, and indirectly by competition for land, water and fertilizers for establishing energy plantations.

Carbon sequestration, by natural or pedologic/engineering/ industrial processes, is directly or indirectly linked to all causes of world's food insecurity. For example, climate change and drought are caused by atmospheric enrichment of CO₂. Soil degradation and nutrient mining/imbalance are caused by depletion of SOC pool by perpetual use of extractive farming practices. Use efficiency of input (*e.g.*, fertilizers, irrigation) can only be increased if SOC pool can be raised above the critical level of 1.1 to 1.2% in the root zone, which in most soils of sub-Saharan Africa and South Asia is presently about 0.1 to 0.2%. Use of nutrient-fortified biochar, a by-product of the pyrolysis of biomass conversion into liquid biofuels, can enhance the SOC pool and improve soil quality.

Enhancing and maintaining soil quality (physical, chemical and biophysical) are essential pre-requisites to sustaining agronomic production to meet the increasing food demands of the world. Restoring and maintaining the SOC pool are essential to improving soil quality. Lal¹⁵⁰ estimated that increasing the C pool in the root zone of world cropland soils can increase food grain production by 32 ± 11 million tons y⁻¹ and root/tuber production by 11 ± 4 million tons y⁻¹. This important inter-connectivity is one of the several reasons why C sequestration in the terrestrial biosphere (especially in world's soils) is called a “win-win-win strategy”. It mitigates climate change by offsetting fossil fuel emissions, improves environment especially the water quality by filtering/denaturing pollutants and by reducing erosion and non-point source pollution, and increases agronomic production by enhancing soil quality and use efficiency of all inputs. Indeed, some have termed atmospheric CO₂ as a misplaced resource. While the CO₂ fertilization effect may contradict somewhat the logic of calling CO₂ “the misplaced resource”, its transfer into soil is definitely beneficial to restoring numerous ecosystem services, the most important of which are mitigating climate change while advancing food security and eliminating of worlds hunger and malnutrition.

X. Conclusions

Transfer of atmospheric CO₂, presently at 780 Pg and increasing at the annual rate of 4 Pg, to other pools (oceanic, geologic, biotic and pedologic) is essential to minimizing the risks of global warming and environmental degradation. Engineering techniques of oceanic and geologic sequestration have a high sink capacity, but are constrained by high costs and risks of leakage necessitating regulatory measures and the establishing of protocols for measurement, monitoring and verification. In addition to injection of CO₂ deep into the ocean, Fe fertilization in the Southern Ocean can enhance “biological pumping” through increased productivity of phytoplankton and other marine biota. Geologic sequestration into oil wells is done to enhance its recovery and in unmineable coal seams to enhance displacement of coal bed methane. In strong contrast to the engineering techniques, there are three natural processes of C sequestration: weathering of Ca/Mg silicate minerals, formation of secondary carbonates, and photosynthesis followed by humification of biomass. Photosynthesis, humification and formation of secondary carbonates increase the terrestrial (soil and biota) C pools. Weathering of silicates and formation of secondary carbonates are slow processes and operate on centennial to millennial (geologic) time scales. Yet, industrial processes of conversion of point-source CO₂ into carbonates is being tried to mimic the natural process.

The pedologic or soil C sequestration has numerous ancillary benefits through restoration of ecosystem services. Important among these are improvement in soil quality, increase in biodiversity, restoration of degraded soils and ecosystem, and reduction in the rate of enrichment of atmospheric CO₂. Improvement in soil quality is essential to enhancing agronomic production but also minimizing soil erosion risks, decreasing non-point source pollution and sedimentation, and reducing risks of hypoxia of coastal ecosystems.

There are specific niches where different sequestration strategies have comparative advantages. While there are challenges and opportunities for each strategy (*e.g.*, geologic, oceanic, terrestrial), the prudent approach lies in identifying which option is environmentally and economically viable under what ecological conditions?

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