

Carbon sequestration

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Developing technologies to reduce the rate of increase of atmospheric concentration of carbon dioxide (CO₂) from annual emissions of 8.6 Pg C yr⁻¹ from energy, process industry, land-use conversion and soil cultivation is an important issue of the twenty-first century. Of the three options of reducing the global energy use, developing low or no-carbon fuel and sequestering emissions, this manuscript describes processes for carbon (CO₂) sequestration and discusses abiotic and biotic technologies. Carbon sequestration implies transfer of atmospheric CO₂ into other long-lived global pools including oceanic, pedologic, biotic and geological strata to reduce the net rate of increase in atmospheric CO₂. Engineering techniques of CO₂ injection in deep ocean, geological strata, old coal mines and oil wells, and saline aquifers along with mineral carbonation of CO₂ constitute abiotic techniques. These techniques have a large potential of thousands of Pg, are expensive, have leakage risks and may be available for routine use by 2025 and beyond. In comparison, biotic techniques are natural and cost-effective processes, have numerous ancillary benefits, are immediately applicable but have finite sink capacity. Biotic and abiotic C sequestration options have specific niches, are complementary, and have potential to mitigate the climate change risks.

Keywords: climate change; greenhouse effect; soil management; geological sequestration; chemical sequestration; oceanic sequestration

1. INTRODUCTION

Global surface temperatures have increased by 0.8°C since the late nineteenth century, and 11 out of the 12 warmest years on record have occurred since 1995 (IPCC 2007). Earth's mean temperature is projected to increase by 1.5–5.8°C during the twenty-first century (IPCC 2001). The rate of increase in global temperature has been 0.15°C per decade since 1975. In addition to the sea-level rise of 15–23 cm during the twentieth century (IPCC 2007), there have been notable shifts in ecosystems (Greene & Pershing 2007) and frequency and intensity of occurrence of wild fires (Running 2006; Westerling *et al.* 2006). These and other observed climate changes are reportedly caused by emission of greenhouse gases (GHGs) through anthropogenic activities including land-use change, deforestation, biomass burning, draining of wetlands, soil cultivation and fossil fuel combustion. Consequently, the concentration of atmospheric GHGs and their radiative forcing have progressively increased with increase in human population, but especially so since the onset of industrial revolution around 1850. The concentration of carbon dioxide (CO₂) has increased by 31% from 280 ppmv in 1850 to 380 ppmv in 2005, and is presently increasing at 1.7 ppmv yr⁻¹ or 0.46% yr⁻¹ (WMO 2006; IPCC 2007). Concentrations of methane (CH₄) and nitrous oxide (N₂O) have also increased steadily over the same period (IPCC 2001, 2007; Prather *et al.* 2001; WMO 2006). Total radiative forcing, externally imposed perturbation in the radiative energy budget of the Earth's

climate system (Ramaswamy *et al.* 2001), of all GHGs since 1850 is estimated at 2.43 W m⁻² (IPCC 2001, 2007).

There is a strong interest in stabilizing the atmospheric abundance of CO₂ and other GHGs to mitigate the risks of global warming (Kerr 2007; Kintisch 2007b; Kluger 2007; Walsh 2007). There are three strategies of lowering CO₂ emissions to mitigate climate change (Schrage 2007): (i) reducing the global energy use, (ii) developing low or no-carbon fuel, and (iii) sequestering CO₂ from point sources or atmosphere through natural and engineering techniques. Between 1850 and 1998, anthropogenic emissions are estimated at 270 ± 30 Pg by fossil fuel combustion and at 136 ± 30 Pg by land-use change, deforestation and soil cultivation (IPCC 2001). Presently, approximately 7 Pg C yr⁻¹ is emitted by fossil fuel combustion (Pacala & Socolow 2004) and 1.6 Pg C yr⁻¹ by deforestation, land-use change and soil cultivation. Of the total anthropogenic emissions of 8.6 Pg C yr⁻¹, 3.5 Pg C yr⁻¹ is absorbed by the atmosphere, 2.3 Pg C yr⁻¹ by the ocean and the remainder by an unidentified terrestrial sink probably in the Northern Hemisphere (Tans *et al.* 1990; Fan *et al.* 1998).

The objective of this paper is to discuss the process and technological options of CO₂–C sequestration in one of the long-lived global C pools so as to reduce the net rate of increase of atmospheric concentration of CO₂. While CO₂–C sequestration is discussed in general, specific attention is given to the terrestrial C sequestration in forests and soils.

2. THE GLOBAL CARBON CYCLE

The importance of atmospheric concentration of CO₂ on global temperature was recognized by Arrhenius

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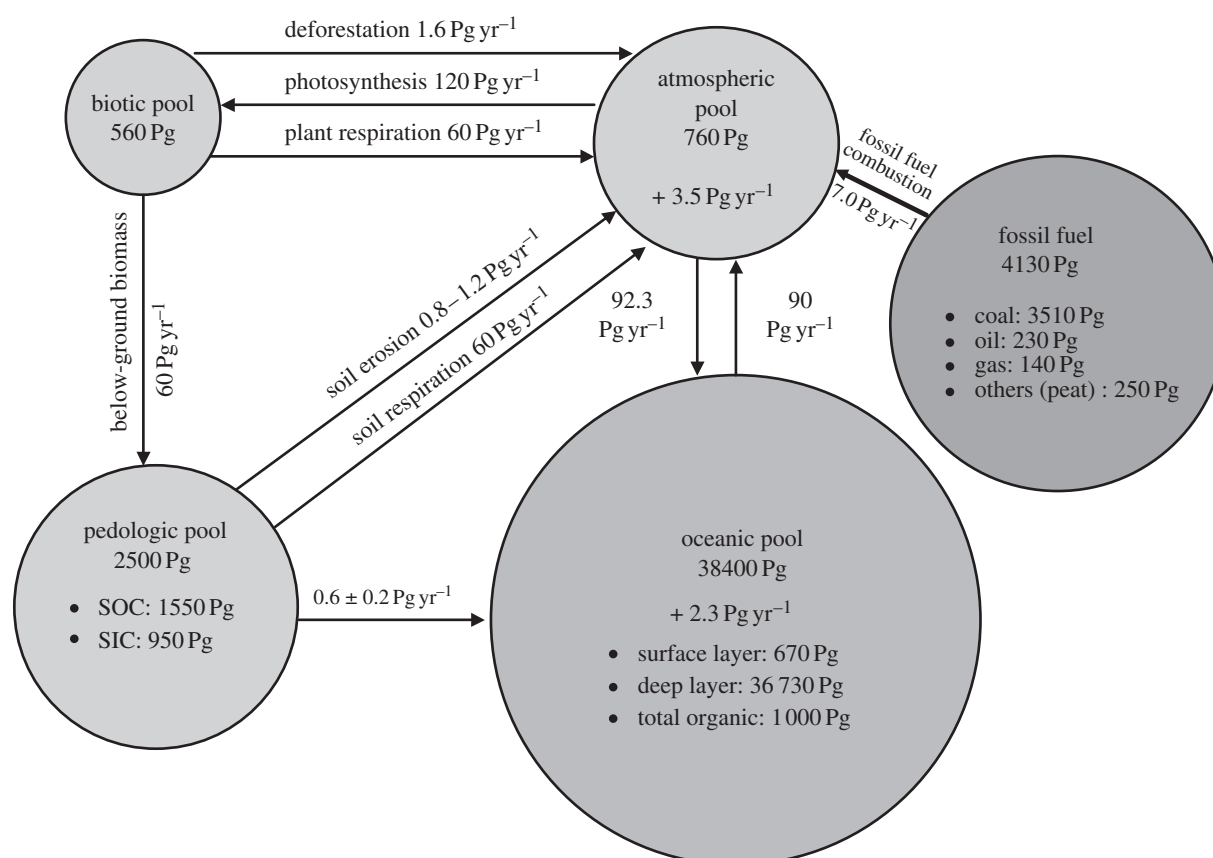


Figure 1. Principal global C pools and fluxes between them. The data on C pools among major reservoirs are from Batjes (1996), Falkowski *et al.* (2000) and Pacala & Socolow (2004), and the data on fluxes are from IPCC (2001).

(1896) towards the end of the nineteenth century, whereas anthropogenic perturbation of the global C cycle during the twentieth century has been an historically unprecedented phenomenon. Understanding the global C cycle and its perturbation by anthropogenic activities is important for developing viable strategies for mitigating climate change. The rate of future increase in atmospheric CO₂ concentration will depend on the anthropogenic activities, the interaction of biogeochemical and climate processes on the global C cycle and interaction among principal C pools. There are five global C pools, of which the largest oceanic pool is estimated at 38 000 Pg and is increasing at the rate of 2.3 Pg C yr⁻¹ (figure 1). The geological C pool, comprising fossil fuels, is estimated at 4130 Pg, of which 85% is coal, 5.5% is oil and 3.3% is gas. Proven reserves of fossil fuel include 678 Pg of coal (3.2 Pg yr⁻¹ production), 146 Pg of oil (3.6 Pg yr⁻¹ of production) and 98 Pg of natural gas (1.5 Pg yr⁻¹ of production; Schrag 2007). Presently, coal and oil each account for approximately 40% of global CO₂ emissions (Schrag 2007). Thus, the geological pool is depleting, through fossil fuel combustion, at the rate of 7.0 Pg C yr⁻¹. The third largest pool is pedologic, estimated at 2500 Pg to 1 m depth. It consists of two distinct components: soil organic carbon (SOC) pool estimated at 1550 Pg and soil inorganic carbon (SIC) pool at 950 Pg (Batjes 1996). The SOC pool includes highly active humus and relatively inert charcoal C. It comprises a mixture of: (i) plant and animal residues at various stages of decomposition; (ii) substances

synthesized microbiologically and/or chemically from the breakdown products; and (iii) the bodies of live micro-organisms and small animals and their decomposing products (Schnitzer 1991). The SIC pool includes elemental C and carbonate minerals such as calcite, dolomite and gypsum, and comprises primary and secondary carbonates. The primary carbonates are derived from the weathering of parent material. In contrast, the secondary carbonates are formed through the reaction of atmospheric CO₂ with Ca⁺² and Mg⁺² brought in from outside the local ecosystem (e.g. calcareous dust, irrigation water, fertilizers, manures). The SIC is an important constituent in soils of arid and semi-arid regions. The fourth largest pool is the atmospheric pool comprising 760 Pg of CO₂-C, and increasing at the rate of 3.5 Pg C yr⁻¹ or 0.46% yr⁻¹. The smallest among the global C pools is the biotic pool estimated at 560 Pg. The pedologic and biotic C pools together are called the terrestrial C pool estimated at approximately 2860 Pg. The atmospheric pool is also connected to the oceanic pool which absorbs 92.3 Pg yr⁻¹ and releases 90 Pg yr⁻¹ with a net positive balance of 2.3 Pg C yr⁻¹. The oceanic pool will absorb approximately 5 Pg C yr⁻¹ by 2100 (Orr *et al.* 2001). The total dissolved inorganic C in the oceans is approximately 59 times that of the atmosphere. On the scales of millennia, the oceans determine the atmospheric CO₂ concentration, not vice versa (Falkowski *et al.* 2000). The link between geological (fossil fuel) and atmospheric pool is in one direction: transfer of approximately 7.0 Pg C yr⁻¹

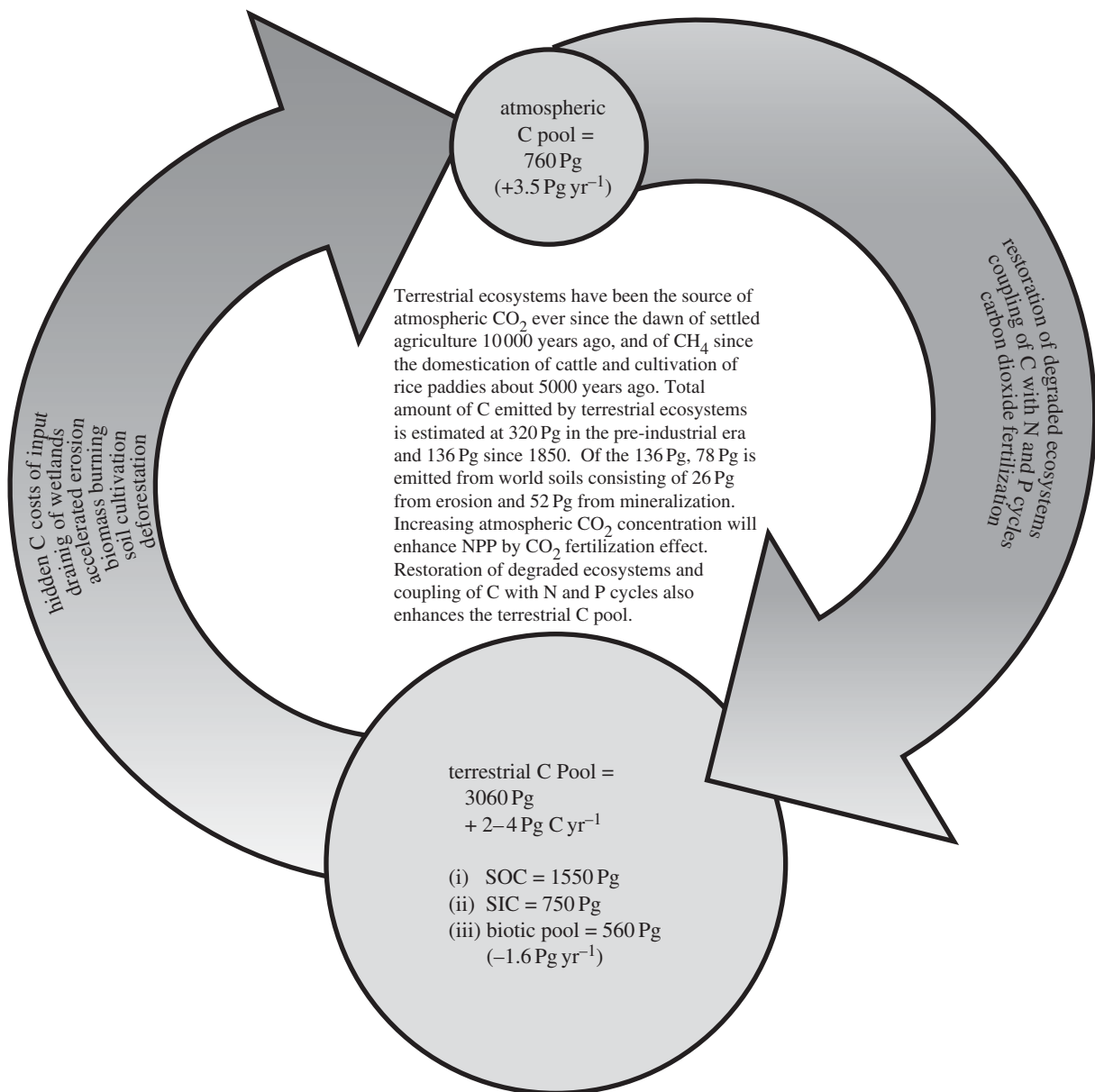


Figure 2. The atmospheric C pool is increasing at the rate of 3.5 Pg C yr⁻¹. The terrestrial C pool contributes approximately 1.6 Pg C yr⁻¹ through deforestation, biomass burning, draining of wetlands, soil cultivation including those of organic soils, accelerated erosion and hidden C costs of input (e.g. fertilizers, tillage, pesticides, irrigation). Terrestrial C pools are presently sink of 2–4 Pg C yr⁻¹. Conversion to a judicious land use and adoption of recommended practices in managed ecosystems can make these important sinks especially due to CO₂ fertilization effects.

from fossil fuel consumption to the atmosphere. The rate of fossil fuel consumption may peak by about 2025.

The terrestrial and atmospheric C pools are strongly interacting with one another (figure 2). The annual rate of photosynthesis is 120 Pg C, most of which is returned back to the atmosphere through plant and soil respiration. The terrestrial C pool is depleted by conversion from natural to managed ecosystems, extractive farming practices based on low external input and soil degrading land use. The pedologic pool loses 0.4–0.8 Pg C yr⁻¹ to the ocean through erosion-induced transportation to aquatic ecosystems. The terrestrial sink is presently increasing at a net rate of 1.4 ± 0.7 Pg C yr⁻¹. Thus, the terrestrial sink absorbs approximately 2–4 Pg C yr⁻¹ and its capacity may increase to approximately 5 Pg C yr⁻¹ by 2050 (Cramer *et al.* 2001; Scholes & Noble 2001). Increase

in the terrestrial sink capacity may be due to CO₂ fertilization effect and change in land use and management. The biotic pool also contributes to increase in atmospheric CO₂ concentration through deforestation and biomass burning.

3. CARBON SEQUESTRATION

Emission rates from fossil fuel combustion increased by 40% between 1980 and 2000 (Wofsy 2001). Yet, the amount of CO₂ accumulating in the atmosphere remained the same over this period because the excess CO₂ released is being removed by oceans, forests, soils and other ecosystems (Battle *et al.* 2000). Atmospheric CO₂ increased at a rate of 2.8–3.0 Pg C yr⁻¹ during the 1980s and 1995, and between 3.0 and 3.5 Pg C yr⁻¹ during 1995–2005. Considering the total anthropogenic emissions of between 6 and 8 Pg C yr⁻¹, while the atmospheric increase has been

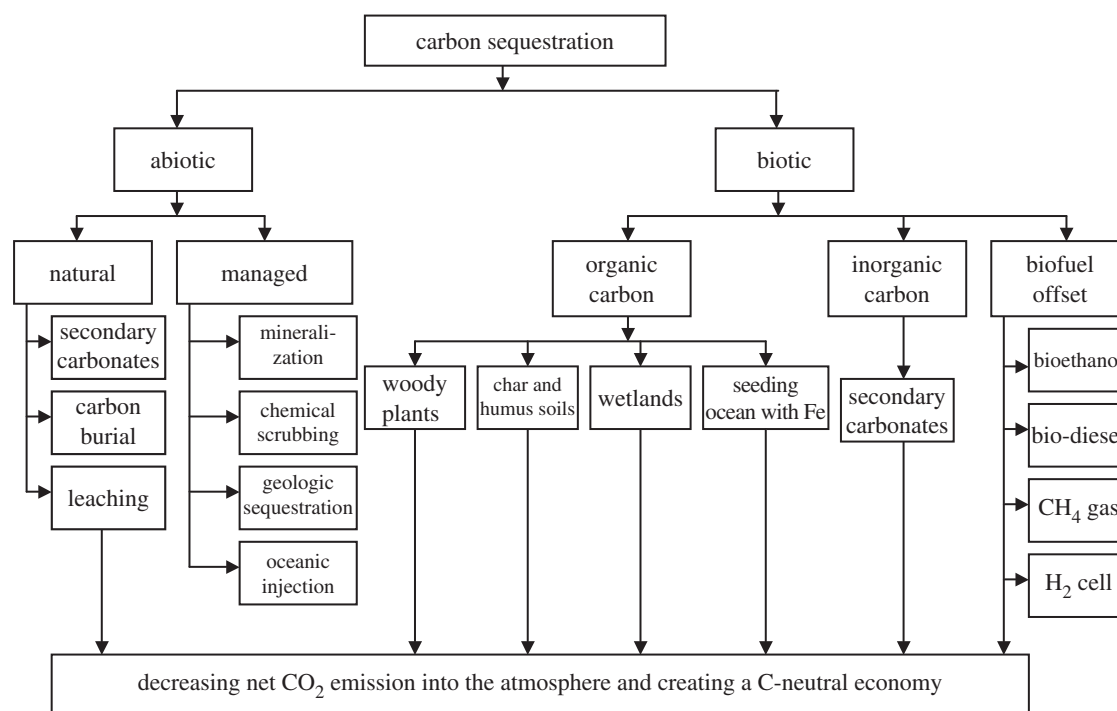


Figure 3. A wide range of processes and technological options for C sequestration in agricultural, industrial and natural ecosystems.

2.8–3.5 Pg yr⁻¹, implies the existence of large global terrestrial sinks (Fung 2000; Pacala 2001). Fan *et al.* (1998) estimated a mean annual uptake of 1.7 ± 0.5 Pg C yr⁻¹ in North America, mostly south of 51° N. In comparison, the Eurasia–North Africa sink was relatively small. This process of transfer and secure storage of atmospheric CO₂ into other long-lived C pools that would otherwise be emitted or remain in the atmosphere is called ‘carbon sequestration’. Therefore, in this context, C sequestration may be a natural or an anthropogenically driven process. The objective of an anthropogenically driven C sequestration process is to balance the global C budget such that future economic growth is based on a ‘C-neutral’ strategy of no net gain in atmospheric C pool. Such a strategy would necessitate sequestering almost all anthropogenically generated CO₂ through safe, environmentally acceptable and stable techniques with low risks of leakage. Lackner (2003) estimated that if a C-neutral strategy is based mainly on sequestration rather than emission reduction, total C storage during the twenty-first century will exceed 600 Pg with residence time of centuries to millennia. However, even a small leakage of 2–3 Pg C yr⁻¹ from the C sequestered in one of the pools can adversely impact the strategic planning for future generations. Pacala & Socolow (2004) outlined 15 options of stabilizing the atmospheric concentration of CO₂ by 2050 at approximately 550 ppm. Of the 15 options, three were based on C sequestration in terrestrial ecosystems.

There are several technological options for sequestration of atmospheric CO₂ into one of the other global pools (figure 3). The choice of one or a combination of several technologies is important for formulating energy policies for future economic growth and development at national and global scales. These

options can be grouped into two broad categories: abiotic and biotic sequestration.

(a) *Abiotic sequestration*

Abiotic sequestration is based on physical and chemical reactions and engineering techniques without intervention of living organisms (e.g. plants, microbes). The abiotic strategy of C sequestration in oceanic and geological structures has received considerable attention (Freund & Ormerod 1997) because theoretically abiotic sequestration has a larger sink capacity than biotic sequestration. Rapid progress is being made in developing/testing technologies for CO₂ capture, transport and injection (Kerr 2001).

(i) *Oceanic injection*

Injection of a pure CO₂ stream deep in the ocean is a possibility that has been widely considered by engineers for about three decades. Following the initial proposal in the late 1970s, there has been considerable progress in oceanic injection of CO₂. To be stable and minimize outgassing, CO₂ must be injected at great depths. Therefore, liquefied CO₂ separated from industrial sources can be injected into the ocean by one of the following four techniques: (i) it is injected below 1000 m from a manifold lying at the ocean floor, and being lighter than water, it rises to approximately 1000 m depth forming a droplet plume; (ii) it is also injected as a denser CO₂–seawater mixture at 500–1000 m depth, and the mixture sinks into the deeper ocean; (iii) it is discharged from a large pipe towed behind a ship; and (iv) it is pumped into a depression at the bottom of the ocean floor forming a CO₂ lake. Liquefied CO₂ injected at approximately 3000 m depth is believed to remain stable (O’Connor *et al.* 2001). The oceanic sink capacity for CO₂ sequestration is estimated at 5000–10 000 Pg C,

exceeding the estimated fossil fuel reserves (Herzog *et al.* 1997, 2002). However, CO₂ injection may also have some adverse effects on deep sea biota (Auerbach *et al.* 1997; Caulfield *et al.* 1997; Seibel & Walsh 2001). In addition to the economics, the issue of stability of such an injection must be addressed owing to the increased stratification of the ocean water column and its turn over through natural processes.

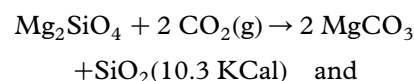
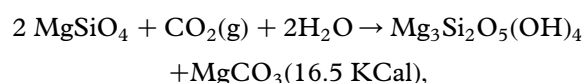
(ii) Geological injection

This involves capture, liquefaction, transport and injection of industrial CO₂ into deep geological strata. The CO₂ may be injected in coal seams, old oil wells (to increase yield), stable rock strata or saline aquifers (Tsang *et al.* 2002; Klara *et al.* 2003; Baines & Worden 2004; Gale 2004). Saline aquifers are underground strata of very porous sediments filled with brackish (saline) water. In general, saline aquifers are located below the freshwater reservoirs with an impermeable layer in between. Industrial CO₂ can be pumped into the aquifer, where it is sequestered hydrodynamically and by reacting with other dissolved salts to form carbonates. Carbon dioxide is injected in a supercritical state that has much lower density and viscosity than the liquid brine that it displaces. *In situ*, it forms a gas-like phase and also dissolves in the aqueous phase, creating a multiphase multicomponent environment. Injecting CO₂ into reservoirs in which it displaces oil or gas could be an economic strategy of enhanced oil recovery (EOR). Production from oil and gas fields, which has been in decline, is raised by CO₂-enhanced recovery (Klusman 2003). This strategy of CO₂ sequestration is used in Texas, USA, to inject 20 million Mg of CO₂ yr⁻¹ at a price of \$10–\$15 Mg⁻¹ (Lackner 2003). The technique is also used in offshore oil wells in Norway. In a strict sense, however, this is not sequestration when the CO₂ injected is extracted from underground wells. The CO₂ can also be injected into unmineable coal seams where CH₄ is absorbed. Injected CO₂ is absorbed onto coal twice as much as CH₄, and the process enhances the gas recovery of coal bed CH₄ (CBM). Principal concerns about geological sequestration, similar to that of the oceanic, are (Kintisch 2007a; Schrag 2007): (i) reliability of storage of vast quantities of CO₂ in geological strata and (ii) the cost. Some have argued that risks of leakage are low. However, to date, a few direct injection of CO₂ have been made on a commercial scale although the Regional Carbon Sequestration Partnership project of US DOE is planning for several demonstrations during 2008–2009. Similar to oceanic injection, cost and leakage are principal issues of geological sequestration which need to be resolved. Owing to the low density and viscosity and injection under supercritical conditions, the risks of CO₂ leakage through confining strata may be higher than currently injected liquid wastes (Tsang *et al.* 2002). In addition, the chemical interactions of CO₂ with the geological formations may have to be considered in formulating guidelines for appropriate regulatory and monitoring controls.

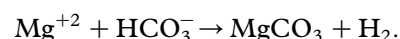
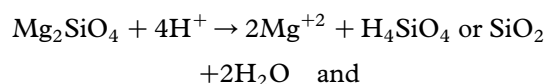
(iii) Scrubbing and mineral carbonation

Mineral carbonation is achieved through mimicry of natural inorganic chemical transformation of CO₂

(Fan & Park 2004). It involves transformation of industrial strength CO₂ emissions into CaCO₃, MgCO₃ and other minerals in the form of geologically and thermodynamically stable mineral carbonates. It is a two-stage process: scrubbing and mineral carbonation. Scrubbing, the process of chemical absorption of CO₂ using an amine or carbonate solvent, is the most widely used method of carbon capture. The CO₂ is purified by passing through an absorption column containing amine solvent. Other solvents used are K₂CO₃, lithium silicate, ceramic and nickel-based compounds. Pure CO₂ gas, recovered by heating the CO₂-rich amine, is re-precipitated through mineral carbonation. Carbonates thus formed are stable rock in which CO₂ is sequestered forever. Aqueous mineral carbonation reactions leading to the formation of magnesite (MgCO₃), olivine (Mg₂SiO₄) and serpentine (Mg₃Si₂O₅(OH)₄) are as follows (Gerdemann *et al.* 2003):



All these reactions occur in nature and can be replicated in industrial settings. The industrial process of mineral carbonation has been described by Lackner *et al.* (1996, 1997) and O'Connor *et al.* (2000). The process uses a slurry of fine particle-sized mineral in water, at solid concentrations of 15–30%. Dissolution of the mineral and subsequent carbonation occur in a single operation as per the following theorized reactions (O'Connor *et al.* 2000; Gerdemann *et al.* 2004):



Geological studies have shown that reserves of ultramafic (ultrabasic) minerals are sufficient to provide raw materials for mineral carbonation of industrial emissions for long time (Goff *et al.* 1997, 2000). However, these are geological reactions and occur at slow rate. The challenge lies in increasing the rate of reaction by decreasing the particle size, increasing temperature and pressure and using catalytic agents (Fan & Park 2004). Increasing the rate of reactions, however, requires energy and is expensive.

(b) Biotic sequestration

Biotic sequestration is based on managed intervention of higher plants and micro-organisms in removing CO₂ from the atmosphere. It differs from management options which reduce emission or offset emission. Increasing use efficiency of resources (e.g. water, energy) is another option for managing the terrestrial C pool (table 1). Some biotic sequestration options are briefly described below.

Table 1. Terrestrial carbon management options.

management of terrestrial C pool	sequestration of C in terrestrial pool
reducing emissions <ul style="list-style-type: none">eliminating ploughingconserving water and decreasing irrigation needusing integrated pest management to minimize the use of pesticides	sequestering emissions as SOC <ul style="list-style-type: none">increasing humification efficiencyimproving soil aggregationdeep incorporation of SOC through establishing deep-rooted plants, promoting bioturbation and transfer of DOC into the ground water
offsetting emissions <ul style="list-style-type: none">establishing biofuel plantationsbiodigestion to produce CH₄ gasbio-diesel and bioethanol production	sequestering emissions as SIC <ul style="list-style-type: none">forming secondary carbonates through biogenic processesleaching of biocarbonates into the ground water
enhancing use efficiency <ul style="list-style-type: none">precision farmingfertilizer placement and formulationsdrip, sub-irrigation or furrow irrigation	

(i) Oceanic sequestration

There are several biological processes leading to C sequestration in the ocean through photosynthesis. Phytoplankton photosynthesis is one such mechanism (Rivkin & Legendre 2001), which fixes approximately 45 Pg C yr⁻¹ (Falkowski *et al.* 2000). Some of the particulate organic material formed by phytoplankton is deposited at the ocean floor and is thus sequestered (Raven & Falkowski 1999). Availability of Fe is one of the limiting factors on phytoplankton growth in oceanic ecosystems. Thus, several studies have assessed the importance of Fe fertilization on biotic CO₂ sequestration in the ocean (Martin & Fitzwater 1988; Falkowski 1997; Martin *et al.* 2002; Boyd *et al.* 2004). It is also argued that incremental C could be sold as credits in the developing global C marketplace. Similar to deep injection, ocean fertilization may also change the ecology of the ocean (Chisholm *et al.* 2001). However, with the current state of knowledge, the topic of ocean fertilization remains a debatable issue (Johnson & Karl 2002).

(ii) Terrestrial sequestration

Transfer of atmospheric CO₂ into biotic and pedologic C pools is called terrestrial C sequestration. Of the 8.6 Pg C yr⁻¹ emitted into the atmosphere, only 3.5 Pg or 40% of the anthropogenically emitted CO₂ remains in the atmosphere primarily owing to unspecified terrestrial sinks which sequester atmospheric CO₂ and play an important role in the global C cycle. Terrestrial ecosystems constitute a major C sink owing to the photosynthesis and storage of CO₂ in live and dead organic matter. Owing to its numerous ancillary benefits (e.g. improved soil and water quality, restoration of degraded ecosystems, increased crop yield), terrestrial C sequestration is often termed as win-win or no-regrets strategy (Lal *et al.* 2003). It offers multiple benefits even without the threat of global climate change. There are three principal components of terrestrial C sequestration: forests, soils and wetlands.

Forest ecosystems store C as lignin and other relatively resistant polymeric C compounds. Presently, the net rate of C sequestration in forest ecosystems (other than those being deforested) is 1.7 ± 0.5 Pg C yr⁻¹

(Fan *et al.* 1998). The forest C is sequestered not only in the harvestable timber, but also in woody debris, wood products and other woody plants encroaching upon grasslands (Wofsy 2001). The terrestrial NPP is not saturated at the current CO₂ concentration and may increase with increase in atmospheric CO₂ concentration through the CO₂ fertilization effect. The NPP may be saturated at 800–1000 ppm of CO₂ concentration (Falkowski *et al.* 2000). Thus, the forest sink may increase by CO₂ fertilization effect (Krishnamurthy & Machavaram 2000). The potential CO₂ fertilization effect may peak during the middle of the twenty-first century (Kohlmaier *et al.* 1998). However, at increasing CO₂ concentration, the NPP may be limited by the deficiency of N, P, H₂O and other factors. Interaction between cycles of C, N, P and H₂O, if moderated through judicious management, may enhance terrestrial C sequestration.

Afforestation is one of the viable options of C sequestration in terrestrial ecosystems (IPCC 1999; Fang *et al.* 2001; Lamb *et al.* 2005). The potential of C sequestration through afforestation is estimated at 3 Tg C yr⁻¹ in Norway, 6 Tg C yr⁻¹ in New Zealand, 9 Tg C yr⁻¹ in Sweden, 107 Tg C yr⁻¹ in Russia and 117 Tg C yr⁻¹ in the USA (IPCC 1999). The rate of C sequestration in US forests, considering all components, is 0.3–0.7 Pg C yr⁻¹ (Pacala *et al.* 2001). Restoration of degraded tropical forest is another important option (Lamb *et al.* 2005). It is estimated that 350 Mha of tropical forest have been converted to other land uses, and another 500 Mha of forests have been degraded to varying extent (Lal 2005a,b,c). Thus, establishment of productive and monoculture plantations of *Pinus*, *Eucalyptus* and *Acacia* can enhance the terrestrial C pool in these ecosystems. There is also a potential for improving the management of secondary or regrowth forests in degraded tropical landscapes. Fang *et al.* (2001) estimated that in China, between 1970 and 1998, C sequestration in forests increased at an average rate of 21 Tg C yr⁻¹ mainly due to afforestation and growth. The total C pool in Chinese forest decreased from 5.1 Pg in 1949 to 4.3 Pg in 1977–1981. Subsequently, it progressively increased during 1980s and 1990s to 4.7 Pg in 1998 (Fang *et al.* 2001). Townsend *et al.* (2002) suggested a sizeable CO₂

uptake in C-3 dominated tropical regions in eight of the 10-year study period. Their data showed a possible existence of a large equatorial terrestrial CO₂ sink.

Pacala & Socolow's (2004) estimated management of temperate and tropical forest is one of the 15 options to stabilize atmospheric CO₂ concentration at 550 ppm by 2050. They estimated that 0.5 Pg C emission would be avoided if the current rate of clear cutting of primary tropical forest were reduced to zero over 50 years by 2050. Another 0.5 Pg C yr⁻¹ would be sequestered by reforestation or afforestation approximately 250 Mha in the tropics or 400 Mha in the temperate zone. An additional 0.3 Pg C yr⁻¹ can be sequestered by establishing approximately 300 Mha of plantations of non-forested lands (Pacala & Socolow 2004). The afforestation may account for a total of 25 Pg C sequestration between 2000 and 2050.

However, afforestation on a large scale can impact water resources. Jackson *et al.* (2005) documented substantial losses in stream flow, and increased soil salinization and acidification, with afforestation. They observed that establishment of tree plantations decreased stream flow by 227 mm yr⁻¹ globally (52%), with 13% of streams drying completely for at least one year. Thus, any plans of large-scale afforestation for C sequestration must consider the possible adverse impact on availability of water.

Bunker *et al.* (2005) addressed the concern of decline in tropical forest biodiversity due to expansion of monoculture plantations. Thus, resulting effects of monoculture plantations on key ecosystem services (e.g. biodiversity, water resources, elemental cycling, C sequestration) must be critically assessed. There is a strong need for developing regulatory policies, including the transaction costs of trading C credits and obtaining the permits. The cost of C sequestration vis-à-vis the opportunity cost must also be considered (McCarl & Schneider 2001).

Wetlands and the associated soils or histosols constitute a large pedologic pool estimated at approximately 450 Pg (Gorham 1991; Warner *et al.* 1993). Wetland soils may contain as much as 200 times more C than the associated vegetation (Milne & Brown 1997; Garnett *et al.* 2001). Gorham (1991) and Kobak *et al.* (1998) estimated that C sequestration in wetlands/peatsoils since the post-glaciation period resulted in the C accumulation at the rate of 0.1 Pg C yr⁻¹ over 10 000–18 000 years. However, drainage of peatlands and their subsequent cultivation made these ecosystems a net source of CO₂. Large areas of wetlands have been drained worldwide for agriculture (Armentano & Menges 1986) and forestry (Paavilainen & Paivanen 1995). Drained wetland soils decompose and subside at the rate of approximately 1–2 cm yr⁻¹ primarily due to oxidation (Rojstaczer & Deverel 1995; Hillman 1997; Wosten *et al.* 1997). Restoration of wetlands can lead to reversal of the process and make restored wetlands once again a sink of atmospheric CO₂. However, there is a long time lag after the restoration until processes in restored wetlands become similar to those of natural wetlands.

Soil C sequestration. Implies enhancing the concentration/pools of SOC and SIC as secondary carbonates through land-use conversion and adoption of

recommended management practices (RMPs) in agricultural, pastoral and forestry ecosystems and restoration of degraded and drastically disturbed soils. Formation of charcoal and use of biochar as a fertilizer is another option (Fowles 2007). In contrast to geological sequestration that implies injecting CO₂ at 1–2 km depth, the SOC sequestration involves putting C into the surface layer of 0.5–1 m depth through the natural processes of humification. Most soils under the managed ecosystems contain a lower SOC pool than their counterparts under natural ecosystems owing to the depletion of the SOC pool in cultivated soils. The most rapid loss of the SOC pool occurs in the first 20–50 years of conversion of natural to agricultural ecosystems in temperate regions and 5–10 years in the tropics (Lal 2001). In general, cultivated soils normally contain 50–75% of the original SOC pool. The depletion of the SOC pool is caused by oxidation/mineralization, leaching and erosion.

Strategies for increasing the SOC pool are outlined in figure 4. There is a wide range of degraded soils with a depleted SOC pool. Important among these are those degraded by erosion, nutrient depletion, acidification and leaching, structural decline and pollution/contamination (figure 4). Restoring degraded soils and ecosystems is a strategy with multiple benefits for water quality, biomass productivity and for reducing net CO₂ emission. Grainger (1995) estimated that there are approximately 750 Mha of degraded lands in the tropics with potential for afforestation and soil quality enhancement. With a sequestration potential of approximately 0.5 Mg ha⁻¹ yr⁻¹ as SOC and an additional 1.0 Mg ha⁻¹ yr⁻¹ as biomass, a terrestrial C sequestration potential of 750 Mha is approximately 1.1 Pg C yr⁻¹. Lal (2001) estimated the SOC sequestration potential of 0.4–0.7 Pg C yr⁻¹ through desertification control in soils of arid and semi-arid regions. Similar estimates were provided by Squires *et al.* (1995).

West & Post (2002) assessed SOC sequestration rate upon conversion of plough tillage to no-till farming through analyses of data of 67 long-term experiments from around the world. They reported the mean rate of SOC sequestration of 570 ± 140 Kg C ha⁻¹ yr⁻¹, which may lead to the new equilibrium SOC pool in 40–60 years. Lal (2004a,b) estimated the global SOC sequestration potential, 0.4–1.2 Pg C yr⁻¹ or 5–15%, of the global fossil fuel emissions. Pacala & Socolow (2004) estimated that conversion of plough tillage to no-till farming on 1600 Mha of cropland along with adoption of conservation-effective measures could lead to sequestration of 0.5–1 Pg C yr⁻¹ by 2050.

Integrated nutrient management (INM) is also essential to SOC sequestration. The humification process can be severely constrained by the lack of N, P, S and other building blocks of soil humus (Himes 1998). The efficiency of C sequestration is reduced when C and N are not adequately balanced (Paustian *et al.* 1997). Therefore, the SOC sequestration rate is enhanced by an increase in the application of biomass C (Campbell *et al.* 1991; Janzen *et al.* 1998) and N (Halvorson *et al.* 1999, 2002). Liebig *et al.* (2002) observed that high N rate treatments increased SOC

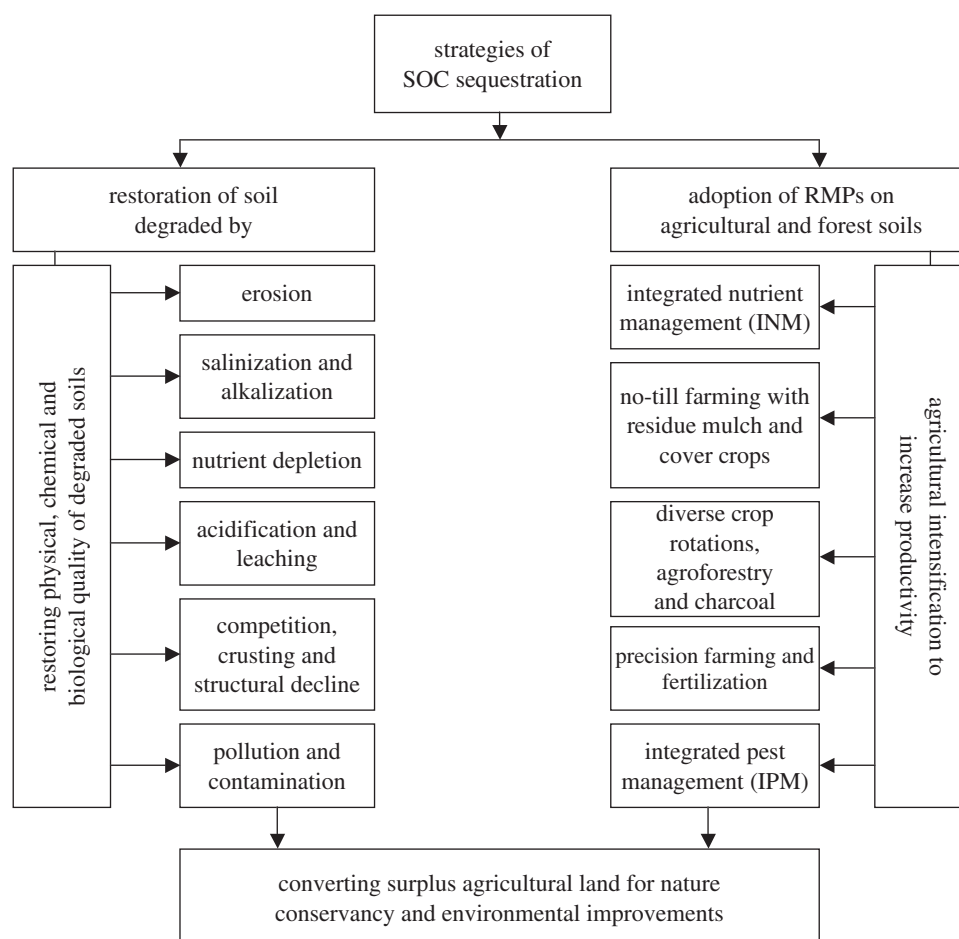


Figure 4. Management strategies for soil carbon sequestration through restoration of degraded soils and adoption of RMPs on agricultural soils.

sequestration rates by $1.0\text{--}1.4\text{ Mg C ha}^{-1}\text{yr}^{-1}$ compared with unfertilized controls. Similar observations were made by Dumanski *et al.* (1988), Schjonning *et al.* (1994), Gregorich *et al.* (1996), Bowman & Halvorson (1998), Studdert & Echeverria (2000), and Jacinthe *et al.* (2002). Malhi *et al.* (1997) reported that SOC sequestration depended both on the rate and the source of N application. In Victoria, Australia, Ridley *et al.* (1990) observed that application of P and lime increased the SOC pool in the 0–10 cm layer by 11.8 Mg ha^{-1} over a 68-year period at an average rate of $0.17\text{ Mg C ha}^{-1}\text{yr}^{-1}$.

Application of manures and other organic amendments is another important strategy of SOC sequestration. Several long-term experiments in Europe have shown that the rate of SOC sequestration is greater with application of organic manures than with chemical fertilizers (Jenkinson 1990; Witter *et al.* 1993; Christensen 1996; Korschens & Muller 1996; Smith *et al.* 1997). Increase in the SOC pool in the 0–30 cm depth by long-term use of manure compared to chemical fertilizers was 10% over 100 years in Denmark (Christensen 1996), 22% over 90 years in Germany (Korschens & Muller 1996), 100% over 144 years at Rothamsted, UK (Jenkinson 1990) and 44% over 31 years in Sweden (Witter *et al.* 1993). The data from Morrow plots in Illinois indicated that manured plots contained 44.6 Mg ha^{-1} more SOC than unmanured control (Anderson *et al.* 1990). In Hungary, Arends & Casth (1994) observed an increase in SOC

concentration by $1.0\text{--}1.7\%$ by manuring. Smith *et al.* (1997) estimated that application of manure at the rate of 10 Mg ha^{-1} to cropland in Europe would increase the SOC pool by 5.5% over 100 years. In Norway, Uhlen (1991) and Uhlen & Tveitnes (1995) reported that manure application would increase SOC sequestration at the rate of $70\text{--}227\text{ Kg ha}^{-1}\text{yr}^{-1}$ over 37–74-year period.

Soils under diverse cropping systems generally have a higher SOC pool than those under monoculture (Dick *et al.* 1986; Buyanoski *et al.* 1997; Drinkwater *et al.* 1998; Buyanoski & Wagner 1998). Elimination of summer fallow is another option for minimizing losses of the SOC pool (Delgado *et al.* 1998; Rasmussen *et al.* 1998). Growing a winter cover crop enhances soil quality through SOC sequestration. In the UK, Fullen & Auerswald (1998) reported that grass leys set aside increased SOC concentration by $0.02\%\text{ yr}^{-1}$ for 12 years. In Australia, Grace & Oades (1994) observed that the SOC pool in the 0–10 cm layer increased linearly with increase in frequency of pasture in the crop rotation cycle. In comparison with continuous cropping, incorporation of cover crops in the rotation cycle enhanced SOC concentration in the surface layer by 15% in Sweden (Nilsson 1986), 23% in The Netherlands (Van Dijk 1982) and 28% in the UK (Johnston 1973) over 12–28-year period. Similar results were reported by Lal *et al.* (1998) for the US cropland.

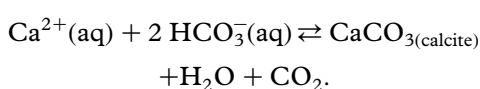
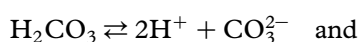
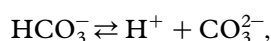
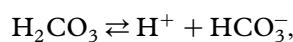
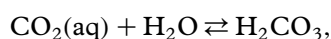
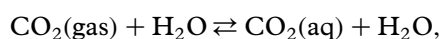
The rate of sequestration ranges from negative or zero under arid and hot climates to approximately

1000 Kg C ha⁻¹ yr⁻¹ under humid and temperate climates (Lal 2004b, 2005a,b,c). Normal rates of SOC sequestration on agricultural soils are 300–500 Kg C ha⁻¹ yr⁻¹. High rates are obtained with no-till farming, crop residue retention as mulch, growing cover crops in the rotation cycle and adopting complex farming systems including agroforestry, INM including manuring and through restoration of degraded soils by afforestation.

Adoption of RMPs on agricultural and forest soils is a win-win strategy (Follett 2001; Lal *et al.* 2003; Lal 2004a,b, 2006). While improving soil quality and agronomic productivity, agricultural intensification through adoption of RMPs also improves water quality, reduces non-point source pollution by decreasing dissolved and sediment loads, and reduces net rate of CO₂ emission through SOC sequestration. It is a very natural process (Morris 2006). However, for the SOC sequestered to be stabilized, it is important to understand the stabilizing mechanisms (Six *et al.* 2002), limitations of biophysical ecosystems in C sequestration (Schlesinger 1999; Sauerbeck 2001), and relevant economic and policy issues (McCarl & Schneider 2001). Trading of C credits may require several permits (at federal, state and local levels) and marketing procedures.

(iii) Secondary carbonates

Soil C sequestration may also occur in SIC as secondary carbonates, and leaching of bicarbonates into the ground water. Secondary carbonates occur in various forms as films, threads, concretions and pedants. They also occur as laminar caps, caliche and calcrete (Gile 1993). In skeletal soils with high gravel concentration, secondary carbonates occur as coatings on lower surfaces of stones and pebbles. There are four principal mechanisms of formation of secondary carbonates (Monger 2002; Mermut & Landi 2006). Marion *et al.* (1985) proposed that secondary carbonates are formed through dissolution of CO₂ in the surface layer followed by translocation and re-precipitation with Ca⁺² and Mg⁺² in the subsoil. In contrast, Sobecki & Wilding (1983) described the second mechanism based on capillary rise of Ca⁺² from shallow ground water and its re-precipitation in the surface layer. The third mechanism of *in situ* dissolution and re-precipitation was proposed by Rabenhorst & Wilding (1986). Monger (2002) observed that pedogenic/secondary carbonates are of biogenic origin and are formed by activity of soil fauna (e.g. termites). Chemical reactions describing the dissolution of CO₂ are shown in the following equations described by Mermut & Landi (2006):



Secondary carbonates are formed in the soil pH range of 7.3–8.5. There must, however, be sufficient quantity of Ca⁺² and Mg⁺² present in the soil system. Decreasing water content, decreasing partial pressure of CO₂ or HCO₃⁻ in soil air, and increasing the products of Ca⁺² or HCO₃⁻ in soil favour the precipitation of secondary carbonates.

In contrast to SOC, the rate of formation of secondary carbonates is low. In the deserts of southwestern USA, Marion *et al.* (1985) estimated that during the Pleistocene the rate of deposition of secondary carbonates was 1.2–6 Kg C ha⁻¹ yr⁻¹. In another study for the same region, Schlesinger (1985) estimated the rate of formation of secondary carbonates as being between 1.2 and 4.2 Kg C ha⁻¹ yr⁻¹. Also in the southwestern USA, Monger & Gallegos (2000) reported the rates of formation of secondary carbonates at 1–14 Kg C ha⁻¹ yr⁻¹. In Saskatchewan, Canada, Landi (2002) estimated the rate of deposition of secondary carbonates ranging between 9.9 and 13.4 Kg C ha⁻¹ yr⁻¹. For a non-calcareous parent material, Machette (1985) estimated the rate of deposition ranging between 1.7 and 6.1 Kg C ha⁻¹ yr⁻¹, and concluded that rates are generally high in calcareous soils.

Leaching of biocarbonates into ground water is another mechanism of transfer of SIC into a less active pool, especially in soils irrigated with good quality water (Nordt *et al.* 2000). The rate of leaching of HCO₃⁻ in irrigated soils may be as much as 0.25–1.0 Mg C ha⁻¹ yr⁻¹ (Wilding 1999). There are 250 Mha of irrigated land area globally. The potential of leaching of HCO₃⁻ in these soils may be 62.5–250 Tg C yr⁻¹. With the exception of irrigated soils, there are not many technological options to enhance the rate of deposition of secondary carbonates. Use of organic amendments (e.g. crop residue mulch, manure and other biosolids) may enhance activity of termites and other soil fauna, and also increase the formation of secondary carbonates through biogenic processes. Use of good quality irrigation water to enhance leaching of HCO₃⁻ is another relevant option for irrigated soils.

4. BIOFUELS

Converting biomass-derived sugars to ethanol and plant-derived oils and fats into bio-diesel is a viable strategy to reduce use of fossil fuels and develop alternate/sustainable sources of energy (Himmel *et al.* 2007; Stephanopoulos 2007; Wald 2007). Of the world's total primary energy supply of 11.2 Pg of oil equivalent in 2004, 35.03% came from oil, 24.6% from coal, 20.44% from gas, 6.33% from nuclear and 13.61% from renewable sources (Goldemberg 2007). Of the renewable sources, 2.48% was contributed by the traditional biofuels (e.g. animal dung, crop residues, wood products), and 1.91% by modern biofuels. Only 3.22% of the primary energy was contributed by hydro, solar, wind and geothermal sources.

Biofuels, high on the political and scientific agenda, are related to C sequestration in two distinct but interrelated aspects (figure 5): (i) soil

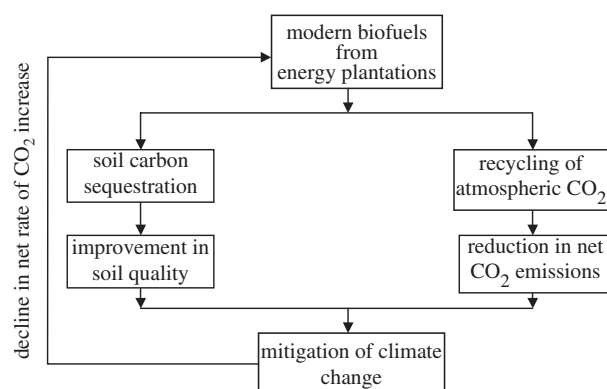


Figure 5. Interactive effects of modern biofuels produced from energy plantations on terrestrial/biotic carbon sequestration.

C sequestration through restoration of the depleted SOC pool, especially when agriculturally degraded/marginal soils are converted to energy plantations, and (ii) recycling of atmospheric CO₂ into biomass-based biofuels. With choice of the appropriate species and prudent management, biofuels produced from energy plantations established by dedicated crops (e.g. poplar, willow, switch grass, miscanthus, karnal grass, *Andropogon*, *Pennisetum*) can sequester C in soil, offset fossil fuel emissions and reduce the rate of abundance of atmospheric CO₂ and other GHGs. In contrast to the beneficial impacts, some have argued that there will be an increase in competition for land and water to establish energy plantations.

With the long-term goal of producing 1 Pg of lignocellulosic biomass in the USA and 4–5 Pg in the World, crop residues (e.g. corn, wheat, sorghum, millet, barley) are increasingly being considered as source of the biomass (Somerville 2006; Graham *et al.* 2007). It is also argued that using corn grain-based ethanol instead of gasoline reduces GHG emissions only by 18% (Service 2007). Thus, ethanol produced from cellulosic biomass rather than grains is a preferred alternative. Furthermore, the price of corn grains has increased to more than \$330 Mg⁻¹ in the USA, which has a snowballing impact on food prices in Mexico and elsewhere. Some countries (e.g. USA, China, India) are planning to use 300–400 million Mg of crop residue per annum as a source of renewable energy, which may have severe adverse consequences on soils and the environment. Indeed, indiscriminate removal of crop residues can severely jeopardize soil quality (figure 6). For example, it has been the perpetual removal of crop residues for numerous competing uses (e.g. fodder, household fuel, construction material) and use of animal dung for cooking fuel which have caused widespread and severe problems of soil degradation, low crop yields, and hunger and malnutrition in South Asia and sub-Saharan Africa (Lal 2006).

Crop residues are not a waste. They are precious commodities and their use as soil amendments is essential for preserving soil quality (Wilhelm *et al.* 2004). Adverse impacts of residue removal on soil quality must be objectively and critically reviewed prior to installing large-scale cellulosic ethanol plants. Thus,

cellulosic biomass must be produced on specifically established energy plantations. It is also possible to procure biomass from low-input high-density (LIHD) mixtures of native grassland perennials (Tilman *et al.* 2006).

5. FARMING CARBON

Carbon sequestered in soils and trees can be traded, just as any farm produce (e.g. corn, milk, meat). Trading C credits is a rapidly growing industry (Gressel 2007; McGowan 2007). The market is well established in Europe (Johnson & Heinen 2004; Brahic 2006) and the USA through Chicago Climate Exchange (Breslau 2006). The 'cap and trade' movement is gaining momentum in the USA (Schlesinger 2006; McGowan 2007). The discussion on this topic is now being focused on policy options for slowing emissions of GHGs (Kerr 2007; Kintisch 2007b). Important among these options are: (i) imposing tax on C emissions called C tax, (ii) providing government subsidies, and (iii) trading C credits. The cap and trade system would ensure the achievement of environment goals. While the market for trading C sequestered in soils and biota is being developed in North America and Europe, the strategy may be extremely beneficial to the resource-poor and small land holders of developing countries of Asia and Africa. Trading C credits can provide a much needed income stream for the farmer, and an essential incentive to invest in soil restoration (e.g. erosion control, irrigation, fertilizers), break the agrarian stagnation and advance food security.

6. MERITS AND LIMITATIONS OF BIOTIC VERSUS ABIOTIC CARBON SEQUESTRATION

Biotic C sequestration, based on removal of atmospheric CO₂ through photosynthesis, is a natural process. The magnitude of CO₂ removal through photosynthesis, in woody plants of managed and natural ecosystems, is likely to increase in the future due to the CO₂ fertilization effect. The process can be managed through input of essential nutrients (e.g. N, P, K, Ca, Mg, S, Zn, Cu, Mo) and management of water. There are numerous ancillary benefits of terrestrial/biotic C sequestration. Important among these are: (i) improved quality of soil and water resources, (ii) decreased nutrient losses from ecosystems, (iii) reduced soil erosion, (iv) better wildlife habitat, (v) increased water conservation, (vi) restored degraded soils, and (vii) increased use efficiency of input. Soil C sequestration, both as SOC and SIC, is also a natural process essential for recycling of elements and water. Similar to the terrestrial pool, increase in the SOC pool also has numerous ancillary benefits affecting local, regional and global processes. Principal benefits of SOC sequestration to soil quality are: (i) improvement in soil structure, (ii) reduction in soil erosion, (iii) decrease in non-point source pollution, (iv) increase in plant-available water reserves, (v) increase in storage of plant nutrients, (vi) denaturing of pollutants, (vii) increase in soil quality, (viii) increase in agronomic productivity of food security, (ix) moderation of climate, and (x) increase

Table 2. Comparative advantages and constraints of biotic versus abiotic options.

parameters	biotic (terrestrial)	abiotic (engineering)
the process	natural (photosynthesis, humification)	engineering (capture and injection)
sink capacity	finite (50–100 Pg)	extremely large (thousands of Pg)
time horizon	immediate, for next 25–50 years	10–20 years from now, for long period
cost	negative, none or low	High
risks		
NPP and biomass yield reduction	minor or low	N.A.
human health	minor to low (agricultural chemicals)	High
environmental	positive effect (win-win, no-regret)	high
leakage	none or small (by ploughing, etc.)	complex and expensive methods
monitoring and verification	simple and routine methods	complex and expensive methods
regulatory measures	monetary incentives may be helpful	legislative and policy measures essential

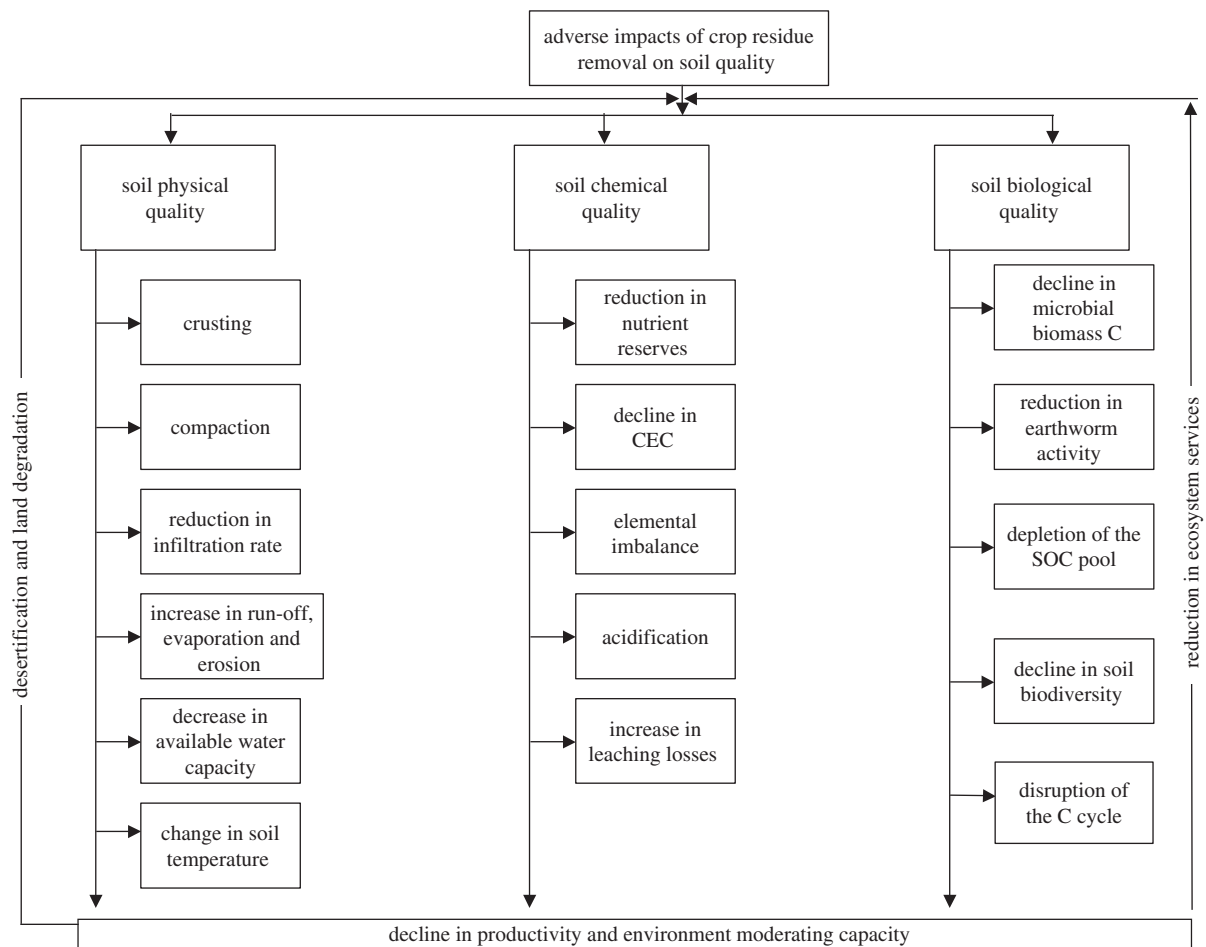


Figure 6. Adverse impacts of crop residue of cellulosic bioethanol production on soil and environment quality.

in aesthetic and economic value of the soil. Therefore, the process of biotic C sequestration strengthens and enhances ecosystem services while enhancing agro-nomic production. The process is cost-effective, and RMPs for adoption on agricultural and forest soils/ecosystem are available for most ecoregions of the world (IPCC 1999). However, the total sink capacity for biotic C sequestration especially that in terrestrial ecosystems is low at 50–100 Pg C over 25–50-year period (Lal 2004a,b). Further, C sequestered in soil and biota can be re-emitted with change in soil management (e.g. ploughing) and land use (e.g. deforestation) (table 2).

In contrast to biotic sequestration, abiotic sequestration is an engineering process. The technology for deep injection in the ocean, geological strata, coal mines and oil wells, etc. are being developed and may be routinely available by 2025 and beyond. At present, these techniques are expensive and injected CO₂ is prone to leakage. In addition to high cost, the issues of measurement and monitoring, adverse ecological impacts and regulatory measures need to be developed and implemented. However, the sink capacity of abiotic techniques is extremely large at thousands of Pg C, and often estimated to exceed the fossil C reserves. Biotic and abiotic systems are complimentary to one another.

Depending upon ecosystem characteristics, there may be site-specific ecological niches for biotic and abiotic sequestration options. Biotic sequestration options are immediately available. Use of such options buys us time, while C-neutral energy production technologies of alternatives to fossil fuels and techniques of abiotic sequestration take effect.

7. CONCLUSIONS

Although natural terrestrial and oceanic sinks are presently absorbing approximately 60% of the 8.6 Pg C yr⁻¹ emitted, natural sink capacity and rate are not large enough to assimilate all the projected anthropogenic CO₂ emitted during the twenty-first century or until the C-neutral energy sources take effect. The sink capacity of managed ecosystems (e.g. forest, soils and wetlands) can be enhanced through conversion to a judicious land use and adoption of RMPs of forestry, agricultural crops and pastures. Purposeful manipulation of biological processes can accelerate the CO₂ sequestration process with adoption of regulatory measures and identification of policy incentives. However, for these management systems to be effective, there is a strong need for an integrated systems approach. While the global C cycle is affected by human activities, it is also coupled with cycles of H₂O and other elements (e.g. N, P, S) and effectiveness of biotic/terrestrial sequestration depends on scientific understanding of these coupled cycles.

Abiotic sequestration of anthropogenically emitted CO₂ through direct injection in oceanic and geological strata has a large sink capacity. Mineral carbonation of CO₂ into stable carbonates of Ca and Mg is another option with a large capacity. These engineering techniques are being developed and may be available for routine use by 2025 and beyond. Additional research is needed to make these technologies cost-effective, reduce leakage risks, minimize any adverse impacts on the environment and enhance safety. In addition to economics, the human dimension issues need to be objectively and critically addressed for both biotic and abiotic CO₂ sequestration options. Appropriate policy and regulatory measures need to be developed, especially with regards to measurement, monitoring, residence time and trading of carbon credits. While carbon sequestration is an important strategy, the significance of reducing emissions through development of carbon neutral technologies cannot be overemphasized. The latter may involve efficient energy production and usage measures, and finding alternatives to fossil fuel. Biofuels (e.g. bioethanol, bio-diesel, methane gas from biodigester and H₂ cell from biomass) are an important component of alternative sources of energy.

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