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#### **Carbon sequestration in soil**

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# ABSTRACT

Carbon (C) sequestration in soil implies transfer and secure storage of atmospheric CO<sub>2</sub> into the soil organic carbon (SOC) pool as recalcitrant humus/biochar, and soil inorganic C (SIC) pool as secondary carbonates. Its importance lies in urgency to off-set increase in atmospheric enrichment of CO<sub>2</sub> from 280 ppm in 1750 to 381 ppm in 2007, and its benefits to agronomic yield and soil quality. The soil C sink capacity, created by the historic land use and soil degradation, is estimated at 78±12 Pg or 10-60 Mg/ha involve: (i) restoration of degraded/desertified soils through conversion to a perennial land use, and (ii) adoption of recommended management practices including no-till farming, manuring, agroforestry and use of biochar as a soil amendment. The mean rate of C sequestration is 300-500 kg/ha/yr for SOC and 2-10 kg/ha/yr for SIC. Accelerated soil erosion is a net source of atmospheric  $CO_2$ , and must be effectively controlled. Soil C sequestration is also enhanced by adoption of nanotechnology, biotechnology, information technology and, trading C credits. Avoidance of deforestation, and afforestation of degraded/desertified soils have a cost-effective and a large potential to off-set emissions, influence the global C cycle, and stabilize the atmospheric CO<sub>2</sub>. Soil C sequestration is a win-win-win strategy because it advances food security, improves the environment and mitigates global warming.

**KEY WORDS**: Trading C credits, global warming, biochar, soil quality, soil restoration, global C cycle, erosion and C cycle

# **INTRODUCTION**

The annual increase in atmospheric abundance of  $CO_2$  depends on the balance between global carbon (C) sources and sinks. Principal sources of CO<sub>2</sub> are fossil fuel combustion and land use change, and sinks are ocean, land and the atmosphere. The schematic and data in Fig. 1 indicate two significant points. One, of the total anthropogenic emissions, only 40 to 45% of CO<sub>2</sub> remains in the atmosphere because oceanic and terrestrial sinks combined absorb the rest even without human intervention. Two, the capacity of the natural sinks, and especially those of terrestrial sinks, has declined during 2000s (Fig. 1, 5) probably because of increase in soil degradation and desertification. For example, the capacity of the natural sinks was 56.3% in 1980s, 60.0% in 1990s and 54.9% in 2000s. Of the total capacity of natural sinks, that of the terrestrial biosphere (land sinks) was 28.2% in 1980s, 27.2% in 1990s and 24.2% in 2000 process of C sequestration implies the transfer and secure storage of atmospheric CO<sub>2</sub> into other long lived C pools through natural or managed processes. Because of the high risks of global warming, there is a strong interest in accentuating the process through transfer of atmospheric  $CO_2$  into oceanic, geologic, biotic and pedologic pools. The wide range of options, including engineering and biotic, are outlined in Fig. 2 and have been discussed elsewhere (e.g., 6). Specifically, C sequestration in soil is the transfer and secure storage of atmospheric CO2 into the pedologic/soil pools, comprising of soil organic C (SOC) and soil inorganic C (SIC) components. Therefore, the objective of this manuscript is to describe processes, factors, causes, strategies and impacts of C sequestration in soils of natural and managed ecosystems

#### SOIL CARBON POOL

The pedologic or soil C pool is the third largest of the five global pools (Fig. 3). Its magnitude of 2500 Pg to 1-m depth is about 3.3 times the atmospheric pool of 760 Pg and 4.0

times the biotic pool of 620 Pg. The soil C pool consists of two distinct components: SOC pool of about 1550 Pg, and SIC pool of 950 Pg, both to 1-m depth (7, 10). The SOC pool comprises any organic C assembly, large or small, dead or = (11), and consists of the following constituents (12; 13): (1) small amounts of plant and animal tissues as remains of the original biomass input, (2) the products of the biological and chemical decomposition of the biomass addition to the soil, (3) living and dead microbial cells, (4) degradation of soil organisms, and (5) interaction products of any or all of these substances. Many of these substances are of colloidal nature and occur in close interaction, both within and outside, of the clay lattices. The SOC pool is often refered interchangeably as soil organic matter (SOM) or humus. While the SOM consists of all five components listed above, humus is a dark brown or black amorphous material. It is highly decomposed component of the SOM, and is characterized by a large surface area, high charge density, high reactivity, and high affinity for the clay fraction. Humic substances are dark-brown organic macro-molecules rich in phenolic compounds and are derived from plant remains and microbial synthesis (14). It is highly dynamic, being simultaneously formed from plant and animal residues, and also decomposed by microbial processes (15, 16). It is the process of decomposition which is the source of energy for all biological processes in soil (17, 18, 19, 20, 21, 22).

The SIC pool, an important component in soils of dry climates, includes elemental C, primary carbonates (e.g., calcite, dolomite, gypsum), and secondary carbonates. The primary carbonates are derived from the weathering of the parent material. In comparison, secondary carbonates are derived from the dissolution of  $CO_2$  in the soil air and the reaction of the weak carbonic acid with  $Ca^{+2}$ ,  $Mg^{+2}$  and other cations brought into the system through atmospheric deposition, run-on, irrigation water, manure and other amendments et plus, soil C

sequestration involves conversion of atmospheric  $CO_2$  into the soil C pool through: (i) addition of biosolids (live or dead) into the soil that eventually go through the process of humification, and (ii) formation of secondary carbonates.

Conversion of natural to managed (cropland, pastureland, woody plantations) ecosystems usually leads to the depletion of the SOC pool (Fig. 4). Most soils lose one-third to one-half of their original pool, and those of the tropics may lose as much as 90% of antecedent pool (23). The magnitude of loss (10-60 Mg/ha) is accentuated when input of C into the managed ecosystem is lower, and losses due to erosion and mineralization are higher than those under prior land use or management. The rate and magnitude of loss are more drastic in the tropics than temperate regions, in coarse-textured than fine-textured soils, in soils with high than low antecedent pool, in well drained than prove to erosion than deposition. Furthermore, the magnitude and rate of loss are more in agro-ecosystems managed with extractive farming practices leading to negative nutrient and water budgets than those managed with recommended management practices (RMPs) which lead to positive nutrient and water budgets. Similarly, the magnitude of the depletion is less in ecosystems converted to an appropriate (as per the land capability assessment) than an inappropriate land use (e.g., conversion to cropland on sloping lands, drainage of peat soils). Depletion of the SOC pool leads to decline in soil quality, and emission of  $CO_2$  and other gases into the atmosphere. Jenny (11) stated that contributions of SOM to atmospheric  $CO_2$  appear underestimated. He argued that "more CO<sub>2</sub> would become oxidized from debris, roots and humus for a number of years after cutting or clearing than would be released promptly by fire and immediate decay". The magnitude of the total loss of SOC pool has been varyingly estimated to range from 40 to 537 Pg, with a mean range of  $78 \pm 12$  Pg (24).

It is this historic depletion of the soil C pool, especially the SOC component, that has created a C-sink capacity in soils of the managed or agro-ecosystems. A goal of soil management strategy is to fill this C-sink capacity through conversion to a restorative/appropriate landuse and adoption of improved or RMPs. Restoration of the SOC pool through C sequestration also leads to improvement in soil quality and resilience.

# **RATIONAL FOR CARBON SEQUESTRATION IN SOILS**

There are numerous reasons for sequestering C in the terrestrial biosphere in general, and in soils in particular. Important among these (e.g., agronomic, ecologic and climatic) are briefly discussed below:

(a) <u>Agronomic Effects of SOC Sequestration</u>: The SOM has been considered as an elixir of plant life ever since the dawn of settled agriculture some 10 to 13 millennia ago. Allison (12) stated that "man has appreciated the fact that dark soils, commonly found in the river valleys and broad level plains, are usually productive soils. He also realized at a very early date that color and productivity are commonly associated with organic matter derived chiefly from decaying plant materials". Lawes and Gilbert (25) observed that a soil with more SOC is a better soil, a more productive soil. Albrecht (26) stated, in the USDA Year Book of Agriculture entitled Soils & Men, that "Soil organic matter is one of our most important national resources; its unwise exploitation has been devastating; and it must be given the proper rank in any conservation policy as one of the major factors affecting the level of crop production in the future". Ever since these visionary statements, the literature is replete with the importance of SOM to enhancing agronomic production and advancing food security (23, 27), especially with the threat of declining crop yield with the projected climate change (28). Lal (29) synthesized the available literature relating crop yield to incremental increase in the SOC pool. He reported that increase in the SOC pool by 1 Mg C/ha/yr can increase crop yield by 20-70 kg/ha for wheat, 10-50 kg/ha/yr for rice, 30-300 kg/ha for maize, 20-50 kg/ha for soybeans and 30-60 kg/ha/yr for beans. This increase in crop yield is due to increase in use-efficiency of input because of improvements in the available water holding capacity, soil structure and aggregation, and cation/anion exchange capacity. Lal estimated that increase in SOC pool by 1 Mg C/ha/yr would increase agronomic production in developing countries by 24-40 million Mg/yr for food grains and 7-11 million Mg/yr of roots and tubers (30). The agrarian stagnation in sub-Saharan Africa and in the dry farming regions of South Asia can only be broken if the soil quality can be improved through increase in SOC pool. As Jenny (14) stated "injecting crop stimulation fertilizers into soil does not recreate soil mass lost or restore natural soil structures and life". Indeed, attempts at increasing production by applying chemical fertilizers to depleted and degraded soils of Africa have met only with modest, if any, success.

The question "should SOC be maintained or increased" must be answered in the context of soil type, land use, and management. Similar to crop seed (e.g., corn, wheat, soybean), SOC is the mean of production as well as an end product. Thus, how much of it must be consumed and how much saved for future use, need a careful appraisal. Tisdale and Nelson (31) stated that all the edaphologically important functions of SOM in soil (e.g., storehouse of nutrients, increase in exchange capacity, source of energy for micro-organisms, improvement in soil structure and tilth, increase in infiltration rate through protection of soil surface against crusting) depend on its decomposition. Thus, they argued, that production of large quantities of biomass (residues) and their subsequent decay is necessary to good crop and soil management. Janzen (32) also debated about the dilemma: can we both conserve organic matter and profit from its decay?. Albrecht (26) wondered about the wisdom of hoarding much SOM "like miser hoarding gold. Organic matter functions mainly as it is decayed and destroyed. Its value lies in its dynamics nature". However, the answer also depends on the level of SOC pool and the critical limit. There exists a critical limit of SOC pool for agricultural soils and this limit may be different for temperate (33) than tropical soils (34). Enhancing SOC pool is essential to improving the use efficiency of input if its level is below the critical limit

# STRATEGIES OF CARBON SEQUESTRATION IN SOIL

Dyson (35) was among the first soil scientists who suggested building upon C reserves in the form of humus. Several reports have since been written about the management systems to build "carbon bank" in soil. Activities and the processes of building the C bank through C sequestration in soils are schematically outlined in Fig. 5. Activities which deplete the SOC pool include deforestation, plowing, extractive farming, negative nutrient budget, uncontrolled grazing, residue removal etc. These activities accentuate soil degradation processes including accelerated erosion, topsoil removal or truncation, mineralization of SOM, loss of nutrients and water out of the ecosystem etc. In these scenarios,  $C_{input} < C_{output}$ , thus  $\Delta$ SOC is negative and the soil C pool is depleted (Fig. 5). In contrast, activities which enhance SOC pool include afforestation, no-till farming (NT), mulching, cover cropping, integrated nutrient management (INM), controlled grazing, agroforestry and liberal use of manure and biosolids. These activities accentuate soil restoration processes including humification, aggregation, illuviation, deposition, strengthening of cycles of H<sub>2</sub>O and elements, and formation of secondary carbonates. In these scenarios, C<sub>input</sub>>C<sub>output</sub>, the  $\Delta$ SOC is positive and the soil C pool is enhanced.

Once C is sequestered in soil it must be secured so that it is not re-emitted to the atmosphere. In addition to increasing  $C_{input}$  over  $C_{output}$ , it is also important that the residence time is increased, through several mechanisms. Important among these are: (i) biochemical

alteration, and (ii) physico-chemical protection (36). The biochemical alteration transforms SOM to chemical forms that are more resistant to decomposition. The physico-chemical protection inhibits biochemical attack by formation of organo-mineral complexes (e.g., stable micro-aggregates). It is the occlusion or encapsulation of decomposable SOM within stable aggregates and its deposition in pores which render it inaccessible to micro-organisms. Improving soil structure and favoring the activities of fungi would increase the residence time of C in soil. Translocation of C deep into the sub-soil, away from the zone of natural and anthropogenic perturbations, is another important strategy (37). Conversion of biomass-C to biochar-C (discussed later) is another option of increasing the residence time.

(a) <u>Soil Organic Carbon</u>: The rate of C sequestration in soil ranges from negative or zero under arid and hot climates to about 2000 kg/ha/yr under cool, humid climates (Table 1, Lal, 23). Most commonly observed rates under on-farm conditions are 300 to 500 kg/ha/yr (Table 1). Higher rates of SOC sequestration are observed in degraded agricultural soils converted to a restorative land use such as perennial cover (e.g., afforestation, improved pasture, in-situ water conservation). Estimates of regional and global potential are summarized in Table 2. For example, the global potential of C sequestration in cropland soils is estimated at 0.4 to 1.2 Pg/yr (23). Pacala and Socolow (9) estimated that conversion of all cropland to NT farming would sequester 1 Pg C/yr. However, only about 100 Mha or 6% of the world's cropland was managed by NT farming in 2007 (114). Stewart et al. (115) concluded that world agricultural soils observe a linear relationship between soil C pool and C input, and saturation of soil C does occur. Therefore, the greatest efficiency in C sequestration is in soils farther from C saturation (e.g., the highly degraded and desertified soils severely depleted of their original SOC pool). The saturation concept was schematically illustrated by Jenny (11), and is graphically depicted in Fig. 5.

(b) <u>Soil Inorganic Carbon:</u> Formation of secondary carbonates is a geologic process, and occurs over a geologic time scale. Thus, the rate of C sequestration as secondary carbonates is lower than that of SOC sequestration, and is usually 2 to 10 kg C/ha/yr (6), but can be as much as 25 kg/ha/yr. In Boreal grassland and forest soils of Canada, Landi et al. (116) reported that the rate of pedogenic carbonate accumulation increases from 12.5 kg C/ha/yr for semi-arid grasslands (Brown soils) to 21.5 kg C/ha/yr for forest soils (Gray soils). Secondary carbonates occur in various forms including films, threads, concretions, pendants, laminar caps, caliche and calcrete. Carbonate pendants are formed in an environment that may contain lithogenic carbonates. Wang and Anderson (117) observed minute crystals (0.5-4 μm in diameter) of secondary carbonates in three chernozemic soils in Saskatchewan, Canada. In the Gangetic Plains of India, Srivastava (118) observed pedogenic/secondary carbonates in the from of dense micrite and diffused needles.

There are numerous factors which affect the process of formation of secondary carbonates (e.g., climate, moisture regime, profile characteristics, and biogenic activity). Formation of secondary or pedogenic carbonates usually occurs in soils with dry or ustic moisture regime, and in those with sudden textural breaks in the lower solum (119). Over the geological time scale, the rate of formation of secondary carbonates was inhibited during the ice age when CO<sub>2</sub> production in soil was low and the water supply was ice-locked. In dry climates, the rate of formation is also limited by high aridity. Indeed, the presence vs. absence of secondary carbonates is a good indicator of paleoprecipitation above or below the annual value of 760 mm (120). Formation of secondary carbonates is accentuated by the presence of biogenic CO<sub>2</sub> source (42). In addition, some soil microorganisms also set-in-motion the process of formation of secondary carbonates. In Spain, Rivadeneyra et al. (121) observed that the presence of *Deleya halophile* enhanced formation of secondary carbonates. The sequential process seemingly commences with a nucleus formed by the aggregation of a few calcified bacterial cells. This is followed by accumulation of more calcified cells and carbonates cement the bacteria together. Rivadeneyra et al. (121) observed that this process leads to the formation of spherical bioliths, and termed it as "biomineralization". Microbial precipitation of dolomite in dilute natural waters was also confirmed in field and laboratory experiment by Roberts et al. (122). Roberts and colleagues observed that methanogens are the dominant metabolic guild and drive dolomite precipitation via nucleation on the cell wall, as another example of biomineralization.

There are two modern application of the natural process of formation of secondary carbonates. One, the strategy of geologic sequestration of  $CO_2$  into the saline aquifer is based on the principle of immobilization of  $CO_2$  through carbonate precipitation (See Fig. 2). For example, Xu et al. (123) assessed the feasibility of  $CO_2$  trapping by secondary carbonate minerals such as calcite, dolomite, siderite and dawsonite in the presence of high pressure  $CO_2$ . They observed trapping capability of 0.5-1.4 kg  $CO_2$ -C (2-5 kg  $CO_2$ )/m<sup>3</sup> of formation. The formation of secondary carbonates into the solid matrix decreased porosity and reduced permeability. Rush et al. (124) also conducted tests to assess the possibility of *in situ* storage of  $CO_2$  in geological strata, particularly in deep brackish to saline non-potable aquifers, as formation of secondary carbonate minerals over time. The data showed mineral dissolution with an increase of desirable ions ( $Ca^{2+}$ ,  $Fe^{2+}$ ,  $Mg^{2+}$ ) in solution that can form the carbonate minerals (e.g., calcite, siderite and magnesite). However, the methodology must be refined if this technology is to be implemented safely, efficiently and predictably (125). Furthermore, the process of  $CO_2$  immobilization through precipitation of secondary carbonates would not occur to permit significant sequestration of  $CO_2$  if few minerals are present in the host rock.

Two, the principles of the formation of secondary carbonates can be used to study geological processes on other planets. For example, Vecht and Ireland (126) hypothesized that occurrence of Vaterite (formation at ~25°C), aragonite (~70°C) and calcite (~80°C) may indicate possible reaction of CO<sub>2</sub> with an aqueous solution of CaCl<sub>2</sub> in the presence of ammonia. These conditions may have existed at the surface of the Mars in the past and imply formation of pseudo-biogenic carbonate structure under exobiology conditions. In contrast, Golden et al. (127) presented experimental evidence that the zoned Mg-Fe-Ca carbonates in a Martian meteorite may have been formed by simple inorganic processes. Gleason et al. (128) studied a Martian meteorite and concluded that complex zoning in carbonates is indicative of non-equilibrium processes in their formation. The data suggested that CO<sub>2</sub>-rich fluids of variable composition infiltrated the rock while on Mars, indicating an inorganic origin of the carbonates.

The formation of secondary carbonates also takes place in building materials when atmospheric  $CO_2$  reacts with  $Ca^{2+}$  present in the pre-solution. Martinez-Ramirez et al. (129) used Mirco-Raman Spectroscopy to establish the existence of various forms of CaCO<sub>3</sub> in fully carbonated lime mortar. Calcite was formed to be the most thermodynamically stable form in the mortar.

#### **BIOFUEL AND CARBON SEQUESTRATION IN SOIL**

The atmospheric concentration of  $CO_2$  has increased from 280 ppm in the pre-industrial era to 381 ppm in 2006 (5). Some consider mitigating the  $CO_2$ -induced climate change as an energy problem (130). In addition to the  $CO_2$ -induced threat of global warming, increase in

price of oil is also the driving force in urgency for developing viable alternatives to fossil fuel, including the biofuel. For example, CO<sub>2</sub>-C emission increased from <0.1 Pg/yr between 1750 and 1799, 0.5 Pg/yr by 1899, to 6.8 Pg/yr by 1999, and is projected to be 12 Pg/yr by 2054 (131). The price of a barrel of oil increased from about \$25/barrel in 2000 to about \$100/barrel in December 2007, which is provoking the new energy crisis (132). The strategies being proposed are mandatory cap on emissions (IPCC meeting in Bali, December 2007), and developing alternate (C-neutral or C-negative) fuel sources. Schlamadinger and Marland (133) suggested that forest and bioenergy strategy offers the prospect of reduced CO<sub>2</sub> emissions through five mechanisms: (i) use of wood products which displace other products that require more fossil fuel for their production, (ii) use of biofuels to displace fossil fuel, (iii) storage of C in forest products, (iv) C sequestration in the forest biomass, and (v) C sequestration in soil. However, the use of biomass as a fuel source has several issues: (i) a low-power density of photosynthesis for biofuels  $(0.6 \text{w/m}^2)$ , thus the need for a large land area (130) along with the competition for water and nutrients, and (ii) the low energy production efficiency. The ethanol production in the U.S. has increased drastically since 2000. It was 1.7 billion gallons (BG) in 2000, 1.9 BG in 2001, 2.1 BG in 2002, 2.8 BG in 2003, 3.4 BG in 2004, 4.0 BG in 2005, 4.9 BG in 2006 and 7 BG in 2007. The 2007 bill mandates 36 BG by 2022, with 21 BG coming from the so-called cellulosic ethanol (134). Thus, there is an urgent need for procuring 1000 billion ton of biomass (135), which has necessitated identifying alternate sources including crop residues (136, 137). In addition to the adverse impact of residue removal on soil quality and non-point source pollution (14, 45, 138), there are also challenges in engineering microbes for production of cellulosic ethanol (139, 140). While ethanol production from sugarcane has been successful in Brazil (141), that from corn grain in the U.S. is debatable (134, 142), and is also a threat to the

Conservation Reserve Program (CRP). Thus, other sources of biomass (e.g., switchgrass or prairie grass) are being considered (143, 144). Pimentel and Patzek (145) observed that ethanol production using corn grain required 29% more fossil energy than the ethanol fuel produced. Establishment of energy plantations (e.g., poplar, willow, miscanthus, switchgrass) may have an advantage of restoring degraded lands and sequestering C in soil while producing biomass. However, the energy efficiency seems to be low with current technology. Pimentel and Patzek (145) estimated that ethanol production required 50% more fossil energy and wood biomass 57% more than ethanol fuel produced from these sources. Scharlemann and Laurance (146) wondered how green are biofuels? It is because of these issues with harvesting crop residues, using soybean/corn grains and establishing biomass plantations that biofuels are considered as "the cure worse than the disease" (147). Some have argued whether expecting food and fuel for all from the scarce land resources is foolish or realistic (148). Others have lamented that there is no such thing as free biofuel from crop residues (149), because removal of crop residues would increase soil erosion risks, increase the need for additional fertilizers, and deplete the SOC pool. Jenny (14) argued against indiscriminate conversion of biomass and organic wastes to fuels. He emphasized that "the humus capital, which is sustainable, deserves being maintained because good soils are national asset". Crop residues can either be used to sequester C in soil or produce ethanol, but not both is either humus or alcohol (14). Furthermore, use of corn and soybeans to produce biofuels is causing food shocks in terms of rising food prices (42). Thus, there is a strong need to identify new strategies of making biofuel which are more economic and efficient. Identifying and harnessing ancillary benefits of biofuel industry may be an important consideration.

Ragauskas et al. (150) emphasized the importance of several by-products of biorefineries. These biomaterials are useful industrial products of economic importance. Use of residues as soil amendments to sequester C in soil is another important consideration. Johnson et al. (151) observed that land application of corn-stover fermentation by-products, which is about 70% lignin, may reduce the environmental risks from crop residue harvest by stabilizing structure and sequestering C in soil.

#### **BIOCHAR AND CARBON SEQUESTRATION IN SOIL**

There is a growing interest in the application of bio-char to soil to improve its quality, sequester C (152), and affect the global C budget (153). The concept is based on the archaeological evidence of a technique developed by pre-Columbian civilization in the Amazon Basin (154). These anthropic soils, developed through enrichment with biochar, are called "terra preta" or dark earth (152). Biochar, charcoal, a biomass-derived black C, can be a long-term sink for atmospheric  $CO_2$  in terrestrial ecosystems. Lehmann et al. (112) observed that conversion of biomass C to biochar C leads to sequestration of about 50% of the initial C compared to the low amounts retained after burning (3%) and the slow process of humification (10-20%). Biochar produces more recalcitrant C which has a long residence time in soil, and as an amendment also leads to immediate benefits to agronomic productivity. Lehmann and colleagues hypothesized that replacement of slash-and-burn agriculture by slash-and-char agriculture could offset as much as 0.2 Pg C annually. Similar conclusions were arrived at by Rumpel et al. (155). Experiment conducted in Central Amazonia by Steiner et al. (156) indicated that recalcitrance of charcoal-C is attributed to the presence of refractory compounds, and its application enhances soil fertility and ameliorates soil quality. Warnock et al. (157) observed that biochar affects microbial population and soil biochemistry, and concluded that biochar

influences mycorrhizal abundance and functioning through the following mechanisms: (i) altering soil physico-chemical properties, (ii) affecting other soil microbial population and activity, (iii) interfering plant-fungus signaling and detoxifying allelochemicals on biochar, and (iv) providing refugia from fungal grazers. While biochar application to soil by itself may not be feasible, its production in conjunction with those of biofuel may be an important strategy of offsetting emission by producing C-neutral fuels.

Production of biochar from residues of forest and animal industry is being done by numerous processes including the Charcoal, Heat and Power (CHaP) process (158); the flash carbonization process by which biomass is converted to biocarbon quickly and efficiently (159); a low cycle time biomass char production systems (160), and a slow pyrolysis system that uses urban and other wastes that cannot be economically recycled or reused (161, 162). Indeed a promising technique to lowering CO<sub>2</sub> in the atmosphere while producing energy is biochar bioenergy based on low temperature pyrolysis (163, 164, 112). The process involves capturing the off-gases from thermal decomposition of biomass to produce energy (heat, electricity or biofuel). Biochar, a major by-product of the process, has many environmental properties. When applied to soil, it has a long residence time, high cation retention capacity, and high absorption capacity. Extracting black C (BC) from biomass can be permanently sequestered as a geomass (165). Thus, the process of char production generates energy while also producing BC which can be used as an amendment to improve soil quality and sequester C in the pedosphere.

Schmidt and Noack (166) listed numerous benefits of using BC, a continuum from partly charred material to graphite and soot particles, to various biological, geochemical and environmental processes including C sequestration in soil. Indeed, BC represents a significant sink in the global C cycle (167, 36, 168, 169), especially a sizeable component of the total C pool

in mixed-grass savanna (169) and in fire-prone ecosystems (170). It represents a major sink of atmospheric  $CO_2$  (171) and has important implications to soil fertility (172). The global rate of BC formation in fire-prone ecosystems is estimated at 50-270 Tg C/yr (171), which is a sink of C because it is highly recalcitrant.

#### SOIL EROSION: A SOURCE OF SINK FOR ATMOSPHERIC CO2

Globally soil erosion affects about 1100 Mha by water and 550 Mha by wind (173), and in the process strongly alters the global C cycle (107). Erosional processes by water runoff and wind preferentially remove SOC because it has low density (0.8-1.2 Mg/m3) and is concentrated in vicinity of the soil surface. Thus, loss of SOC on highly erodible soils is more than the loss due to mineralization (174), and the sediments transported by water and wind are enriched by 2 to 30 time as much SOC as contained in original soil (107). The SOC translocated by erosion is redistributed over the landscape, some of it is buried in depressional sites and the other is carried into the aquatic ecosystems (175, 176, 177). That is why the SOC concentration is more in soils of the foot slopes those on summit or side slopes (175, 178). It is estimated that global soil erosion by water annually transports 4-6 Pg C (107) and is an important factor that affects the global C cycle (179). Yet, the fate of the erosion-displaced SOC is a debatable issue. Sedimentologists argue that it is a C sink (180 190, 191, 192, 193, 194, 195) by as much as 1.5 Pg/yr on a global scale. Van Oost et al. (196) have estimated that the sink capacity of the erosional process on a global scale is only 0.12 Pg/yr. In contrast, agronomists and soil scientists believe that soil erosion is a major source of  $CO_2$  (197). Lal (107) calculated that of the 4-6 Pg C/yr displaced by water erosion, 2.8-4.2 Pg C/yr is redistributed over the landscape, 0.8-1.2 Pg C/yr is emitted into the atmosphere, and 0.4-0.6 Pg C/yr is transported to the aquatic ecosystems and burial sites.

The change in SOC pool over a watershed can be described as per Eq. 1:

$$\Delta \text{ SOC} = \text{SOC}_a - \text{SOC}_f = (D_b + B_a) - (O_i + O_l + O_d + O_r) + A_n \dots Eq. 1$$

Where SOC<sub>a</sub> is the antecedent pool, SOC<sub>f</sub> is the final pool,  $\Delta$  SOC is the change in SOC pool following an erosional event, D<sub>b</sub> is deep burial in protected and depositional sites, B<sub>a</sub> is transport and eventual burial into the aquatic ecosystems, A<sub>n</sub> is the new accumulation over the watershed. The term O refers to oxidation in situ (i), over the landscape (l), in depressional sites including methanogenesis (d), and in rivers and other water bodies (r). An important component that can make  $\Delta$  SOC positive or lead to SOC sequestration is A<sub>n</sub>. It implies that the erosional event can lead to SOC sequestration if A<sub>n</sub> is more after than before the event implying that eroded soils have more NPP than uneroded soils. This is precisely the assumption made by Smith et al. (195) and Stallard (194) under the term "dynamic replacement". However, the NPP of eroded soils is usually lower than those of uneroded soils even with the additional input of fertilizer, irrigation and tillage, all of which have high hidden C costs.

Soil erosion is a 3-phases process: detachment, transport and redistribution, and deposition. While the C is protected against mineralization during the depositional phase, it is exposed to microbial processes and climatic factors during the detachment and transport/redistribution phases. With low NPP of eroded soils and a long time lag (decades) to restoration, the net effect of erosion is an increase in emission, making erosion a net source of atmospheric CO<sub>2</sub>.

# MODERN SCIENTIFIC INNOVATIONS: NANOTECHNOLOGY, BIOTECHNOLOGY, AND INFORMATION TECHNOLOGY

Nanotechnology is defined as utilization of structure with at least one dimension of nanometer size (10<sup>-9</sup>m) for the construction of material, devices or systems with novel or

significantly improved properties due to their nano-size (198). Nanotechnology has numerous applications in agriculture (199), especially in nanofertilizers and nano-delivery systems of nutrients to plant roots which enhance NPP and the amount of biomass-C added to the soil. They can also be used as sorbents of environmental contaminants (200). Lombi et al. (201) have used nano x-ray fluorescence and nano x-ray absorption near-edge structure (n-xanes) to study distribution and exchangeability. Using nanosensors, which can detect soil quality as an index of SOC pool and flux, is an emerging field (202, 203). In combination with remote sensing technology, use of nanosensors can assess edaphic parameters in areas with poor accessibility. Zeolite materials, natural or synthetic, can be used to enhance nutrient and water retention and for use as a soil amendment for slow release of nutrients (204, 205, 206, 207). Zeolites are strong soil modifiers (208). Weak hydrogen bonds with framework oxygen atoms implies that the  $NH_4^+$  molecule can be easily exchanged or desorbed. This property is attractive for agronomy and soil remediation (209, 210). Hydrogels and zeolites can be used to enhance soil water holding capacity (211, 212), and enhance C-input into the soil. Nanofilms, used appropriately, can prevent escape of H<sub>2</sub>O molecules from plants without inhibiting the CO<sub>2</sub> exchange.

Biotechnology has numerous applications to C sequestration in soil through genetically modified (GM) plants with a favorable root:shoot biomass ratio, high concentration of recalcitrant compounds with a long residence time, and tolerance to biotic/abiotic stresses. Plants under stress can emit molecular based signals (213) which can be detected using nanosensors and remote sensing technology, and targeted treatment imposed prior to strong adverse impact on NPP. The GM plants can be developed which are characterized by nanometer-scale pores called protein channels as biosensors (214). Forest biotechnology has numerous applications in C sequestration (215). In combination with nanotechnology, GM trees can have recalcitrant compounds (e.g., phenolics, seuberin) included in the cell to enhance the residence time of C. Advances in information technology and creating digital highways can enhance connectivity and provide the information about modern innovation to farmers in remote areas. Creation of automated decision support systems can promote extension services for resource-poor farmers in developing countries. Wireless transmitters based on solar power is an innovation to promote connectivity among and within rural communities (216). Farmers in developing countries can leap frog to modern innovations that enhance C sequestration in soils and biota by using improved/GM crops and earning extra income through trading C credits.

# PROMOTING CARBON SEQUESTRATION IN SOIL THROUGH CARBON TRADING

The potential of C sequestration in soils is the largest and challenge the greatest in severely eroded, degraded and desertified ecosystems where the extractive farming is the norm. Resource-poor small land holders of the tropics do not have the financial capability to invest in soil restoration. The required input, if available, are prohibitively expensive. However, generating another income stream for farmers through trading of C credits can promote adoption of technology that enhance C sequestration in soils. Carbon trading can be done under the Clean Development Mechanism (CDM) of the Kyoto Protocol (217, 133, 218, 219 through U.N. Organizations (220), and industry (221) such as the Chicago Climate Exchange (222) and the European Exchange (223). Broecker (224) proposed a global C-pie as a tool to stabilize atmospheric CO<sub>2</sub>. The magnitude of C-Pie is computed by assessing the surplus C that must be off-set through emission trading. The surplus is computed on the basis of the desired level of CO<sub>2</sub> concentration in the atmosphere (e.g., 560 ppm) by a specific time (e.g., 2100). Assuming that 4 Pg of C absorbed by the atmosphere equals 1ppm of CO<sub>2</sub> concentration, the global C pie is

720 Pg [(560ppm-380ppm) x 4 Mg/ppm=720 Pg]. The total quota of 720 Pg can be allocated to different countries on the basis of their population. Any country that has a surplus quota beyond its industrial/developmental needs can sell it to others. Developing countries can also trade C sink in soil (and trees) as viable strategies to offset emissions under CDM. However, commodification of C sequestered in soil requires development of a methodology to assess changes in C Pool ( $\Delta$ SOC=kg/ha/yr) over a short period of 1-2 yrs. Furthermore, the SOC pool must be measured over landscape, watershed, farm or regional scale with reference to a baseline (e.g., conventional tillage vis-à-vis no-till). Trading of C credits may be facilitated by imposition of emission taxes and caps (225), and creation of a mechanism to aggregate SOC pool for the participating community. In addition to the baseline (226), the issue of net C sequestration must also be resolved with reference to: (i) the hidden C costs of all input (227, 108), and (ii) emission of all greenhouse gases (e.g., CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) (228). The depth of SOC measurement (to at least to 1-m) is also critical.

## THE COST-CURVE FOR CARBON SEQUESTRATION IN SOIL

Operationalizing the process of trading of C sequestered in soils would need estimate of the cost incurred per unit quantity (Mg). An estimate of the cost may be done as follows: Cost (Mg)=(C<sub>r</sub>-C<sub>c</sub>)/ $\Delta$ SOC ...Eq. 2

Where  $C_r$  is the cost of all inputs required for the RMP (e.g., no-till),  $C_c$  is the cost of all input used for the conventional or reference system also termed baseline (e.g., conventional till), and  $\Delta$ SOC is the change in soil C pool (Mg) over the specified period. The  $\Delta$ SOC must be the net gain in due consideration of N<sub>2</sub>O and CH<sub>4</sub> fluxes, and the hidden C costs of all input. The cost of capital equipment (e.g., no-till seeder, herbicide applicator) must be allocated appropriately considering the expected life of the equipment. Since RMPs are not necessarily adopted for C sequestration but to enhance agronomic yield, total agronomic production in each of the system must also be considered. While the price of C is low in the Chicago Climate Exchange (\$2/Mg of CO<sub>2</sub> in Dec. 2007), C sequestration in soil may also become economically profitable with possible emission tax and cap in the future. The resolution adopted at the IPCC meeting in Bali, Indonesia (Dec. 2007), is a step in that direction. Enkvist et al. (229) and McKinsey and colleagues (230) estimated comparative cost of each possible method of reducing emissions. They developed an integrated fact base and related cost curves showing the significance and cost of each available approach. They observed that a substantial share of the overall opportunities, including a large potential to reduce emission by protecting and replanting trees, lies in developing countries. Furthermore, power generation and manufacturing industry offer less than half of the potential of reducing emissions, and about 25% of a possible reduction would occur from energy conservation (e.g., insulation of the buildings).

The option of protecting and replacing trees in developing countries identified by Enkvist et al. (229) has two components of the terrestrial biosphere: (i) tree biomass, and (ii) soil. Afforestation of degraded/desertified soils in developing countries has a potential to sequest 0.9-1.9 Pg C/yr (231). Restoration of these degraded ecosystems is a matter of urgency for economic, ecologic and environmental reasons. It is a truly win-win strategy. While sequestering C in soil to mitigate the climate change, it increases biodiversity, improves the environment, and advances the food security.

#### CONCLUSIONS

The importance of C sequestration to manage soil fertility has been recognized for millennia, since the dawn of settled agriculture. However, its impact on the atmospheric chemistry as a source of atmospheric  $CO_2$  and its role in stabilizing atmospheric chemistry as a

natural C sink gained attention during 1970s. As the third largest global pool, the soil/pedologic C pool plays an important role in the global C cycle through natural and anthropogenic changes in both organic and inorganic components. The maximum or potential soil C sink cprity is equivalent to the historic C loss estimated at  $78 \pm 12$  Pg. The realizable potential, however, may

Harnessing the potential of C sequestration in soil necessitate addressing several issues through research and development. Important among these are the followings:

(i) identification of soils and ecoregions with high C sink capacity

(ii) validation and adaptation of those land use and management technique which create a positive ecosystem C budget ( $C_{input}>C_{output}$ ),

(iii) assessment of the net C gain in the soil in consideration of all gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O),hidden C costs of input, and the baseline,

(iv) evaluation of C gain intensity in relation to NPP, agronomic productivity and other ecosystems services,

(v) determination of permanence or residence time of C in soil,

(vi) establishment of relation between SOC pool and soil quality,

(vii) development of a routine methodology to measure SOC pool at landscape, farm or watershed scale non-destructively and economically,

(viii) creation of a modus operandi to trade credits of C sequestered in soil and provide incentive to farmers for investments in soil restoration,

(ix) identification of mechanisms of C sequestration (e.g., aggregation, humification, illuviation, recalcitrance) under soil-specific conditions, and managing soils to enhance these processes, and

(x) development of a holistic approach to soil C management involving INM, manuring, biofuel production plication of amendments (biochar) and use of modern innovations such as nanotechnology, biotechnology and information technology.

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Fig. 1 Estimates of anthropogenic sources and sinks, and annual increase in atmospheric C pool. The data in (parenthesis) is the annual increase (ppm/yr) in atmospheric CO<sub>2</sub> (Data based on IPCC, 2000, 2001, 2007; WMO, 2006; Canadell et al., 2007; Marland et al., 2007).



Fig. 2 Processes and practices of C sequestration in soil vis-a-vis other global C pools.



Fig. 3 The soil carbon pool and its interaction with other global carbon pools. All figures are in Pg of C (data on pools from Batjes, 1996; Falkowski et al., 2000; Pacala and Socolow, 2004).

Figure 4



Fig. 4 The ecosystem C pool (trees and soil) captured under the natural vegetation cover (I) and depleted with conversion to agricultural ecosystems (II). The sum of A (soil) and B (trees) represent the potential ecosystem sink capacity. Adoption of RMPs at time T commences to sequest C in soil.



Fig. 5 The soil carbon (C) pool is in a dynamic equilibrium with activities and processes which affect input into and output from the soil ecosystem (SOC is soil organic C, K is decomposition constant, h is humification constant, and A is the addition of biomass to the soil. At equilibrium, when  $\Delta$  SOC = 0, C in soil = hA/k).

#	Location	Soil/Region	Management	Soil	Duration	Carbon	Reference
				Depth (cm)	(Yr)	Sequestration Rate (kg/ha/yr)	
1	USA	Minesoil, Ohio	Reclamation	30	20-25	1480-3160	38
2	Sweden	Climate transect	Afforestation	-	-	150-400	39
			(Norway spruce)				
3	Sweden	Boreal/Temperate	Forest	-	-	40-410	39
4	World	161 sites	No-Till	-	25-30	400-480	40
5	Switzerland	Central Plateau	Intensive	-	3	570-1470	41
			management				
6	USA	North America	No-Till	-	-	0	42
7	Brazil	Cerrado	No-Till	20	25	300-600	43
8	U.K.	Scotland	Peat soil	-	1000	140-720	44
9	USA	Ohio	Mulching	50	10	1200-2200	45
10	Norway	Southern region	Tillage/fertilization	12-24	50	72-370	46
11	USA	Columbia	N fertilization,	-	-	500-1500	47
			rotation				
12	Canada	Saskatchewan	No-Till	15	11	3200-3500	48
13	Canada	Saskatchewan/Chernozem	Eliminating fallow	15	17	135-441	49
14	Brazil	Rainforest	No-till	30	-	270-4000	50
15	Spain	Northwest	No-Till	5	-	1240	51
16	USA	Ohio	No-Till	30	30	433	52
17	USA	Minnesota	No-Till	50	23	0	33
18	Norway	Askov region	Manuring	20	10-16	440-2600	54
19	USA	California	Irrigation	2 m	75	0.1-1	55
						(Carbonates)	
20	Tropics	Africa/LA	Manuring	-	50	80-170	56
21	Caribbean	Tropics	Rotation/Tillage	30	10	200-2000	57
22	USA	Southeastern	No-Till	-	5-15	420	58
			Cover cropping	-	5-15	530	
			Cropping intensity	-	5-15	220	

 Table 1 Rate of carbon sequestration in soils with improved management

			N fertilizer	-	5-15	240	
			Poultry manure	-	5-15	720	
			Forages	-	15-32	1030	
23	USA	Southern Piedmont	No-Till	-	7-10	490	59
24	USA	Indiana	No-Till	100	28	357-821	60
25	Belgium	Southern	Grassland	30	50	438	61
26	USĂ	Appalachian region	No-Till, manuring	30	60	417	62
27	Burkina	Savanna soil	Manuring	30	13	690	63
	Faso						
28	USA	Minesoils, Ohio	Reclamation	30	20-50	700-3000	64
29	USA	Illinois	N fertilization	30	23	158-324	65
30	Canada	Prairie	Rotation	20	-	300	66
31	USA	California	Cropping systems	-	10	(-350)-560	67
32	India	Himalayan	Manuring	45	33	900	68
33	Ethiopia	Southwestern	Afforestation	-	-	1000-3200	69
34	China	Northern	No-Till	5	5	0	70
35	USA	Colorado	Forest	1	-	576-805	71
36	Italy	Northeastern	Manuring	-	25	400	72
37	Canada	Ontario	No-Till	20	11	0	73
38	Costa Rica	Rainforest	Agroforestry	-	10	600	74
39	USA	Midwest	No-Till	100	24	1790	75
40	-	River Basin Scale	Modeling	-	-	60-150	76
41	U.K.	Rothamsted	Afforestation	30	100	400	77
42	USA	Colorado	Native grass mix	20	-	1400-1520	78
43	Australia	Victoria	Phosphorus	10	68	174	79
44	USA	Iowa/Mollisol	N Fertilization	-	12	Negative	80
45	Brazil	Parana	No-Till	20	20	500-800	81
46	USA	Great Plains	No-Till	5	5	294	82
47	Tajikistan	Sierozen	Mulching	50	15	1260-3950	83
48	Norway	Southern region	Crop rotation/ley	20	37	325	84
			farming				
49	Belgium	Cropland	Manuring/mulching	-	20	94	85
50	Australia	Brisbane	Tillage/Rotation	10	20-25	100-1600	86

51	Argentina	Pampas	No-Till	-	-	(2760,	87
						cumulative)	
52	Italy	Southern Alps	Pastures	-	62	360	88
53	Senegal	Peanut Basin	Agroforestry	-	25-50	120-220	89
54	Norway	Southern region	Residue	20	43	104-114	90
55	Norway	Southern	Manuring	20	37-74	68-227	91
56	USA	Ohio/Minesoil	Reclamation	30	50	64-2400	92,93
57	World	276 paired data	No-Till, Crop	-	-	$570 \pm 140$	94
			rotation				
58	World	276 paired data	Rotation	-	-	$200 \pm 120$	94
59	USA	Texas	No-Till	15	20	(47-62 %)	95
60	Brazil	Acrisol/Southern	No-Till	20	18	190-650	96

# Table 2 Potential of soil carbon sequestration

#	Location	Soil/Region	Management	C Sequestration Potential	Reference
				(Tg C/yr)	
1	USA	Central Region	Elimination of fallow	6.2	97
2	Brazil	Cerrado region	Improved management	42	98
3	Amazon	Rainforest	Improved management	508	50
4	South America	Pampas	No-till farming	9.4-12.5	99
5	Mexico and Central	Agricultural soils	Soil/crop management	3.8-16.7	100
	America				
6	Caribbean	Agricultural soils	Soil management	6.5-7.5	57
7	USA	Grazing land	Pasture management	17.5-90.5	101
8	EU countries	15 countries	Improved management	16-19	102
9	USA	Forest land use	Forest management	48.9-185.8	103
10	WANA	Dryland	Improved management	200-400	104
11	World	Tropical soils	RMPs	278-516	105
12	China	Agric. soils	Improved management	112-236	106
13	World	Arid lands	Afforestation	900-1900	107
14	Central Asia	Dry lands	Improved management	10-22	108
15	World	Cropland soils	Improved	400-800	23
16	India	Agric. soils	Improved management	39-49	108
17	Tropical forest	Forest ecosystem	Improved management	200-500	109
18	Europe	Agricultural soils	Improved land use and	70-190	110
			RMPs		
19	USA	Cropland	Improved	144-432	111
20	World	Slash and burn	Biochar	210	112
21	Sub-Saharan Africa	Agricultural land	Soil and crop	28.5	113
		use	management		