Carbon fluxes in soil: long-term sequestration in deeper soil horizons

John F. McCarthy
(Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, Tennessee, USA)

Abstract: Terrestrial ecosystems represent the second largest carbon reservoir, and the C balance in terrestrial ecosystems can be directly impacted by human activities such as agricultural management practices and land-use changes. This paper focuses on the C-sequestration in soil. Although many studies showed that the concentration of SOC is much higher in the shallow soils (0-30 cm), the deeper horizons represent a much greater mass of soil and represent a huge C-storage pool. The process of preferential retention of more strongly adsorbing components, along with competitive displacement of weakly binding components are the key processes that enhance the movement of organic carbon to deeper soil horizons. DOC represents the most dynamic part of organic carbon in soils, and thus can be used as a timely indicator of the short-term change of C-sequestration. Long-term experiments have demonstrated that higher SOC levels in shallow soils would lead to increased fluxes of DOC to deeper horizons, but more data on a wider range of soils and treatment strategies are needed to fully evaluate the linkages between changes in SOC in shallow soil, vertical fluxes of DOC to deeper soil horizons, and enhanced C-inventories in deeper, slow-turnover SOC pools.

Key words: carbon flux; SOC; DOC; land use and management
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1 Introduction

Earth's atmosphere is being significantly altered by human activities. Fossil fuel use and land-use changes are driving the ongoing, rapid rise in atmospheric CO$_2$ and other so-called greenhouse gases. Concerns about the potential effects on regional and global climate motivate this workshop on flux observations. While research on atmospheric fluxes is obviously critical, it is also important to consider ways in which C might be sequestered in long-term storage pools, thus potentially delay or offsetting increases in atmospheric CO$_2$. Terrestrial systems represent the second largest carbon reservoir. Although soil-vegetation C pools are small compared to the oceans, they are potentially more labile in the short-term. Furthermore, the C balance in terrestrial systems can be directly impacted by human activities such as agricultural management practices and land-use changes.

This contribution will focus on C-sequestration in soil. It is appropriate to first place soil organic carbon (SOC) within the context of a global strategy for C budgets, and present preliminary estimates of the impact of soil-C management on the predicted trajectory of global C inventories. More specific studies will then be discussed demonstrating how changes in land use and agricultural management have increased the storage of SOC in the upper soil zone. Saturation of the sorption capacity of the upper soils leads to the downward transport of significant fluxes of dissolved organic carbon (DOC) that can be re-captured and sequestered in deeper soil horizons. Perhaps even more than the ocean and atmosphere, measuring C fluxes in soils presents scientific and logistical challenges, and I will describe one approach to instrumenting an established, long-term field site to collect soil water in deep horizons.

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Author: John F. McCarthy, Ph.D., specialized in global change. E-mail: Jmccartl@utk.edu
2 Strategies for carbon sequestration in soil

Although soil is the second largest C reservoir, the fluxes of SOC are much smaller than, for example, atmospheric C fluxes. Nevertheless, man has managed soil systems for thousands of years, and there is a wealth of studies both on basic soil chemistry and physics, as well as agricultural and biosystems engineering. This wealth of experience and expertise makes it feasible to devise and implement changes that could impact C storage in longer-term C-pools in soil. Post and Kwon (2000) estimated magnitude of potential C-sequestration in soil that could be realized by altered land use management involving conversion of some croplands to forestland or grassland. They conducted an extensive literature survey of published studies on C-inventory changes, and found that the land-use changes resulted in an increase in C-storage that averaged 300 Mg-C km\(^{-2}\) yr\(^{-1}\). Obviously, this is far below the level of C sequestration required to solve the problem of rising atmospheric CO\(_2\) concentrations. However, proper C-management in soils could be an effective strategy to mitigate CO\(_2\) increases in the next 20-100 years (Figure 1; Rosenberg and Izaurralde, 2001). This simulation indicates that implementing soil management could delay the projected increase in atmospheric CO\(_2\) for more than 50 years. The major increases in global CO\(_2\) after the middle of this century can be addressed only through development and implementation of larger scale strategies such as disposal or CO\(_2\) in oceans or deep geological repositories, or technological solutions to prevent increased production and release of CO\(_2\). These technological solutions are still in early developmental stages and cannot be implemented for tens of years, but sequestration in soil can buy time for development until then.

3 Potentials of deep soil horizons for C–sequestration

Most studies of SOC concentrations focus almost exclusively on the upper 15-30 cm of the soil. This is the zone that is more important to evaluating agriculture and land-use management. However, from the global C cycle perspective, it is crucial to include the entire soil profile (Figure 2). As shown by Batjes (1996), the upper soil horizon contains less than one-third of the total inventory of soil organic carbon. Although the concentration of SOC is much higher in the shallow soils, the deeper horizons represent a much greater mass of soil, and thus represent a huge C-storage pool.
The results of Batjes (1996) demonstrate that deeper soil horizons represent a poorly understood, but potentially critical, sink for C-sequestration. Conceptually, enhancing the movement of organic carbon to deeper soil horizons involves several key processes. The first involves implementation of some strategies to increase SOC levels in upper horizons. As SOC concentrations in the shallow soil horizons increase, SOC binding sites on soil will become filled, eventually exceeding the capacity for adsorbing additional SOC inputs. As a result, organic matter will desorb and be transported downward with infiltrating water in the form of DOC. The deeper soil horizons contain less SOC, so the occupied binding sites on those mineral surfaces will re-capture the organic matter, resulting in a gradual increase of the C-pool in the entire soil profile.

4 Mechanisms controlling soil C transport to deep soil horizons

This paper focuses on strategies to enhance C storage in deeper soil horizons. Two key questions must be resolved to achieve this objective. First, what is the potential for promoting vertical transport of organic C from shallow soils for subsequent capture and storage in long-terms C pools in deeper soil horizons? To what extent, by what mechanisms, and over what time-frames can such strategies increase the total inventory of soil C? The second issue concerns the problem of discerning whether a given management strategy is having the desired impact on soil C pools. Because soil C concentrations can be very heterogeneous even over small spatial scales, it is difficult to statistically demonstrate short-term increases or decreases in C inventories at an experimental site. Then, are there surrogate measurements that could function as relatively short-term indicators of long-term changes in soil C pools?

4.1 DOC transport: preferential adsorption and competitive exchange

As mentioned, in the absence of physical mixing of soil (e.g., cultivation), deepening of SOC profiles in soil will occur primarily through mobilization and vertical transport of DOC. While the fundamental processes involved in DOC dynamics, such as competitive sorption, microbial degradation, and oxidative polymerization, are recognized, the manner in which they interact to enhance or suppress sequestration in deeper soils is not well known. To understand the mechanism for the release and subsequent re-adsorption of DOC, it is critical to recognize that natural organic matter is not a defined chemical structure, but rather a complex assemblage of heterogeneous moieties that differ with respect to molecular size, structure and functional group composition. Within this assemblage, some components are preferentially adsorbed to the surfaces of soil particles, while others that have a lower affinity for binding can be competitively displaced by moieties with higher binding affinities. This concept has been demonstrated both in controlled laboratory studies (Dunnivant et al., 1992; Gu et al., 1996a, b) and in field-scale DOC transport experiments (McCarthy et al., 1996). A mathematical model that includes the process of competitive binding of DOC components was demonstrated to yield much better descriptions of observed transport behavior than models that treated DOC as a single component (van de Weerd et al., 1997; 1998). Thus, as new SOC is formed in surface soils due to effective management strategies, binding sites in the upper horizons become saturated, resulting in preferential release of less-strongly adsorbing components. The DOC mobilized in this way becomes a source for adsorption in deeper zones. The process of preferential retention of more strongly adsorbing components, along with competitive displacement of weakly binding components, continues in progressively deeper horizons. Natural or anthropogenic changes in soil- and soil solution chemistry can also impact the magnitude and rate of these processes. For example, nitrogen additions using urea or ammonium nitrate can increase soil pH in the upper horizons, and that change in pH will promote desorption of organic matter. Phosphate acts as a competitive anion for DOC sorption, and may therefore also enhance mobilization of DOC through the soil. Additions of Ca\(^{2+}\) might enhance DOC retention by promoting aggregation and deposition of the organic matter. However, the conjugate anion may counteract this effect. For example, lime (CaCO\(_3\)) would increase pH, whereas sulfate in gypsum (CaSO\(_4\)) would compete
for sorption sites (Jardine et al., 1989).

4.2 DOC as an indicator: sensitivity to the short–term change of C–sequestration

This process of competitive exchange of organic moieties with different soil binding affinities can potentially be utilized as a tool to assess the magnitude and direction of changes in soil organic matter. Because DOC represents the most dynamic part of organic carbon in soils, long-term trends in soil carbon storage should be first revealed by changes in the production, fate and transport of DOC. For example, large molecular weight, aromatic-rich components of DOC are known to have a higher affinity for sorbing to soil than do low molecular weight, hydrophilic components (Dunnivant et al., 1992, Gu et al., 1994, 1996a, b; McCarthy et al., 1996). Thus, deepening of the soil C profile will be presaged by gradual shift in chemistry of DOC to favor those moieties with more strongly-adsorptive characteristics. Such changes would be evident long before statistically measurable changes in SOC levels could be discerned, and thus can be used as a timely indicator for optimizing C sequestration strategies.

5 Enhanced C–sequestration and DOC fluxes under alternate crop management systems

The processes discussed are being examined in long-term experiments on sustainable agriculture (Farm Systems Trial (FST), Rodale Institute, Kutztown, Pennsylvaniia, USA). The experimental site covers 6 ha and consists of randomized, complete block design. Details of the experimental design and farming practices are described elsewhere (Liebhardt et al., 1989). Briefly, three management systems were examined. In one set of randomized plots, crops were fertilized using typical chemical fertilizers ("Conventional"), while two other sets of plots used organic fertilizers, either by periodic incorporation of legumes into the crop rotation ("Legume"), or by addition of composted cattle manure ("Manure"). The FST treatments began in 1981, and maintained consistent management history for approximately 20 years. Twelve plots within each treatment were instrumented with zero-tension lysimeters. Intact soil core lysimeters were designed to minimize disturbance of the soil within and around the lysimeters. The lysimeters were located at a depth of 1 m below the ground surface (Moyer et al., 1996). The lysimeters were 1 m in diameter (surface area of 0.45 m²) to address concerns about the impact of small-scale spatial heterogeneity in the soil.

The changes in SOC concentrations during the first 15 years of the experiment are shown in Figure 3 (left panel; Drinkwater et al., 1998). It is apparent that implementation of sustainable agricultural management practices (Legume and Manure) resulted in significant increases in the SOC inventories in the upper 15-cm of soil. Incorporation of manure lead to greater increases in SOC levels than did rotations using legumes. Drinkwater et al. (1998) attribute this to differences

![Figure 3](image-url) Changes in SOC levels and DOC fluxes at the FST
Left panel: The % change in SOC levels from 1981 to 1995; data from Drinkwater et al. (1998);
Right panel: Annualized flux of DOC collected in 1-m deep lysimeters from 1999-2001
in the composition of the organic amendments.

The flux of DOC transported to a 1-m depth in the soil was calculated from measurements of the volume and DOC concentration of soil water leachate collected in the zero-tension lysimeters (Figure 3, right panel). The data reflect the results of approximately 3 years of continuous sampling, and are expressed in terms of an average annual flux (kg-C ha\(^{-1}\) yr\(^{-1}\)). The higher fluxes observed for the Manure and Legume treatments are consistent with our hypothesis that higher SOC levels in shallow soils would lead to increased fluxes of DOC to deeper horizons.

The quality of the DOC in the leachate also differed among the three treatments. The aromatic content of the DOC was estimated based on UV absorptivity at 272 nm (A\(_{272}\)). Absorbance in this spectral region reflects pi-pi* interactions of aromatic compounds, and has been correlated with the aromatic content of organic matter (Traina et al., 1989). After an extended period of warm, dry conditions in the summer, leachate collected after a storm event in September contained levels of aromatic-C in the Manure plots that were 30% or 40% that in the Legume and Conventional plots, respectively.

The results of these experiments show that inputs of organic fertilizers increase the flux of DOC collected in lysimeters at 1-m depth, and that observed changes in DOC composition suggest that high-affinity binding sites are becoming saturated in response to enhanced SOC levels. However, more data on a wider range of soils and treatment strategies are needed to fully evaluate the linkages between changes in SOC in shallow soil, vertical fluxes of DOC to deeper soil horizons, and enhanced C-inventories in deeper, slow-turnover SOC pools. Further, the use of compositional changes in DOC chemistry as a short-term indicator of the extent and direction of the response of SOC inventories to land management strategies will require more extensive, long-term studies.

6 Challenges to "engineering" soil management for C–sequestration

Although the preliminary results from the Rodale FST are encouraging, it is important to recognize the difficulties of predicting the results of any land use or land management changes. The success of any strategy will be subject to the net impact of a variety of complex interactions among competing soil processes. One example of the unexpected consequences of a seemingly reasonable management strategy is an attempt to increase crop production at the Heilongjiang Agricultural Reclamation Bureau in the highly productive northeastern province in China. This example was provided by Dr. Jie Zhiang, who conducted research at this site before moving to his current position at the University of Tennessee. To enhance soil C levels and increase fertility, agricultural management practices were changed by plowing the plant residue from the wheat/soybean rotation into the soil after harvest, rather than removing them from the fields. On the face of it, it would appear to be a logical strategy based on well-established agronomic principles. However, a series of soil and hydrologic interactions lead to an undesirable result. First, the addition of the organic amendments resulted in an increase in soil porosity. In this humid area of China, the higher porosity leads to an increase in the flux of water through the soil. As a result, base cations were leached from the rooting zone, and, as a consequence, a decrease in soil pH to a level that was below the optimal range for crop production. The net effect of a seemingly "good idea" was a net decrease in crop production, even though the goal of higher SOC levels was achieved. This example illustrates the difficulty in predicting, a priori, the integrated effects of complex soil chemical, physical, and hydrologic interactions.

7 Concluding remarks

This paper has emphasized the role of soil in global C fluxes and C-management strategies. Soils can be readily manipulated using well-established methods, and SOC levels can respond to changes in agronomic management in time-frames that can help ameliorate the anticipated short-term increases in atmospheric CO\(_2\). It is important, however, to extend our thinking about
SOC inventories to include consideration of soil horizons below the shallow rooting zone. C-sequestration strategies would be most effective if they promoted long-term C-storage in deep horizons where SOC turnover is slow.

The good news is that there is a robust body of experience to draw from. China, for example, has a history of soil management going back thousands of years. The research infrastructure already exists in the form of an extensive network of agricultural research stations. These field sites are conducting numerous long term experiments of different management alternatives that can be exploited with a new focus on C-sequestration. Thus, there is great potential for significant and timely impact on global C-fluxes in the next 20-50 years that will be required before larger-scale C storage, such as injection of C in the oceans or geological repositories, can be perfected and deployed.

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