SOIL CHANGE AFTER THREE DECADES OF CONVENTIONAL TILL, NO-TILL, AND FOREST SUCCESSION IN THE PIEDMONT OF GEORGIA, USA

by

SCOTT DEVINE

(Under the Direction of Daniel Markewitz)

ABSTRACT

In the Piedmont of Georgia, a long-term experiment between conventional (CT) and no-till (NT) agriculture has provided insight into the effects of tillage on biogeochemical cycles and soil structure. In this study, adjacent land undergoing forest succession (FS) was added to the agricultural comparison to assess effects on soil organic carbon (SOC), acidification, and aggregation. Three decades of NT and FS have led to similar contents of SOC that exceeds the content under the CT profile (0-2 m) by 20%. Accumulation of carbon in forest biomass relative to CT or NT vastly exceeds SOC differences. Forest uptake of exchangeable soil cations and agroecosystem fertilization explain a deep soil acidification that has occurred under FS. Compared to CT, aggregate stability has improved to a depth of 5 cm under NT and to 28 cm under FS. Forest soil processes can produce water-stable aggregates within a year that may be linked to SOC stabilization.

INDEX WORDS: agroecosystem, no-till, conventional tillage, forest succession, soil organic matter, particulate organic matter, carbon, acidification, aggregates, biogeochemical

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CHAPTER I

INTRODUCTION

This research explores and describes the effects of land use on biogeochemical cycles and full soil profile (0-2 m) properties at Horseshoe Bend (HSB), a long-term research site that compares no-till and conventional tillage management in the Piedmont of Georgia, USA. Early studies from the HSB agroecosystem experiment sought to examine the hypothesis that no-till agroecosystems are more similar to natural ecosystems in terms of efficient nutrient cycling (House et al., 1984; Stinner et al., 1984). Results from these studies gave partial support to their hypothesis, as leaching of some nutrients (calcium and nitrogen) increased from old-field succession to no-till to conventional tillage with the greatest leaching rates. Later studies found that no-till systems also store more organic carbon in the upper 15 cm due to protection from decomposition within water-stable soil aggregates (Beare et al., 1994a; Beare et al., 1994b).

In this thesis, I once again add to the comparison land undergoing forest succession adjacent to the agroecosystem experiment to see whether divergent processes identified in early HSB studies have resulted in differences in soil carbon content and composition, nutrient availability, nutrient leaching rates, and alteration of soil structure. In Chapter II, I review the literature concerning land use effects on soil organic carbon (SOC) dynamics, soil acidification, and alteration of soil structure as it relates to the protection of soil organic matter from decomposition. In Chapter III, data is presented on total SOC, particulate organic carbon (POC), and fine carbon concentrations and contents to 2 m, dissolved organic carbon (DOC) fluxes at three different depths, and an aggregate stability metric to 28 cm. Mechanisms of SOC change are discussed as they relate to changes in SOC fractions, DOC fluxes, and previous research at HSB. In Chapter IV, data is presented on soil acidity and exchange chemistry to 2 m, anion and cation concentrations in solution at three depths in the soil profile, and forest nutrient uptake. A mass-balance approach is then used to trace the causes of the observed differences in exchangeable cations and soil acidity to three mechanisms: (i) transfer of exchangeable cations from the soil to storage in forest biomass; (ii) leaching losses; and (iii) applications of fertilizer to the agroecosystem. In Chapter V, SOC, POC, and fine C concentrations are reported for wet-sieved, aggregate size fractions to 28 cm. Results from a soil-moving experiment are also presented in which destructured soil was placed under the different land uses for a year to examine short-term recovery of structural stability and differential protection of SOC from decomposition after crushing large macroaggregates.

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CHAPTER II

LITERATURE REVIEW

Soil organic carbon

Soil organic carbon (SOC) represents an important global pool of C. There is an estimated 1500 Pg of SOC globally (Lal, 2004). SOC or soil organic matter (SOM), however, is not only a storehouse for C but a critical soil fraction that functions as: (1) the primary soil medium through which N is stored and made available to plants; (2) a soil particle binding agent that affects soil erosion, water infiltration and water holding capacity; and (3) a pH dependent, chemically active surface area that enhances cation exchange capacity, as well as the retention of organic and metallic contaminants. So, while much recent research emphasizes the role of SOC in carbon sequestration, there is an implicit acknowledgement that SOC is involved more broadly in cycling of C and ecosystem function.

Research on the effects of cultivation on SOM in Georgia, USA, goes back at least 50 years. The deleterious effect of cultivation on SOM concentrations to a depth of 90 cm in two common southeastern soil series were shown when forested land is converted to agricultural use (Giddens et al., 1957). While the concentration differences they published are more dramatic above 20 cm, their data suggests that efforts to estimate the effects of agriculture on SOM should not be limited to examination of the plow layer alone. They also sampled twenty-eight pairs of forested and adjacent cultivated soils across all physiographic provinces of Georgia to a depth of approximately 15 cm and reported that cultivation resulted in an average carbon concentration loss of 57% (mean SOM of forest = 3.29% and mean SOM of cultivated soils = 1.43%). If normalized for effects of bulk density, the difference would be less dramatic on a content basis, since surficial forested soils are reported to have lower bulk densities than adjacent cultivated soils (Markewitz et al., 2002). A global review of paired cultivated and undisturbed soils shows that 20 to 40% of SOM is lost in tilled soils, concluding that most of the SOM is lost within the first few years after beginning cultivation (Davidson and Ackerman, 1993). From these studies, one might hypothesize that a general cessation of tillage and a return of perennial vegetation will restore SOM levels to pre-disturbance status.

Indeed, a review of studies documenting changes in soil carbon with conversion of agricultural lands to forest and pasture found rates of accumulation of -47 to 310 g C m^{-2} yr^{-1} during forest establishment (avg. 33.8 g C m^{-2} yr^{-1}) and -90 to 113 g C m^{-2} yr^{-1} during pasture establishment (avg. 33.2 g C m^{-2} yr^{-1}) (Post and Kwon, 2000). Low levels of SOM accretion under afforestation have been reported in the southeastern Piedmont. Four decades of loblolly pine growth on land previously cultivated for cotton found marginal increases in soil C of 4.1 g C m^{-2} yr^{-1} to a depth of 60 cm, reporting significant increases from 0-7.5 cm but significant decreases from 35-60 cm (Richter et al., 1999). The authors speculated that marginal soil C increases were a result of favorable conditions for decomposition due to a combination of the warm southern US climate, the coarse-textured and well-aerated A horizon, and mineralogy unfavorable for physico-chemical protection of soil C (Richter et al., 1999).

Long-term experiments that monitor changes in levels of SOC in relation to land treatments are valuable tools for understanding how management decisions will influence future soil fertility and SOC storage. An excellent record of SOC concentrations to a depth of 21 cm was begun in 1982 at the Horseshoe Bend (HSB) agroecosystem experiment in Athens, GA, USA (Figure 3.1). In an analysis of the data through 1991, Hendrix (1997) concluded that while the no-till (NT) system maintained significantly higher SOC concentrations in the upper 5 cm, SOC concentrations were found to be slightly higher from 5-21 cm under conventional tillage (CT) due to vertical redistribution. Therefore, there was a non-significant difference in SOC content of 4 Mg C ha^{-1} from 0-21 cm. Interestingly, a net loss occurred in both systems from 1982 to 1991: a 25% loss in CT (9 mg C ha^{-1}) and a 15% loss in NT (5 Mg C ha^{-1}). It is possible that this loss was even greater, since SOC concentrations were not measured during the first four years of the experiment.

Subsoil C

A review comparing NT and CT management clearly demonstrates the benefits of NT systems on carbon contents from 0-10 cm (West and Post, 2002). However, in another recent review comparing no-tillage to full-inversion tillage (i.e. moldboard plowing), SOC concentrations were higher just below the plow layer in many of the conventional tillage systems, which was attributed to repeated transfer of surficial crop residues to the depth of soil inversion (Angers and Eriksen-Hamel, 2008). Nevertheless, for soils sampled to ≥ 30 cm in their review, no-till soils still showed a small, but significant ($p=0.03$) net increase of 4.9 Mg C ha^{-1} (100.3 vs. 95.4 Mg C ha^{-1}).

In yet one more review of broader and deeper land use effects on SOC found that concentrations can change significantly to a depth of 100 cm, but that deeper changes depended upon a number of factors, notably the type of land use conversion, vegetation, and climate (Guo and Gifford, 2002). Significant subsoil C decreases between 1 and 3 m depth have also been shown to occur when grasslands are invaded by woody vegetation (Jackson et al., 2002).

Subsoil C is not inherently recalcitrant; its protection may be linked to physical occlusion in large peds that turn over slowly compared to A horizon structural units which experience more frequent bioturbation in unmanaged systems (Ewing et al., 2006). Mechanisms of potential subsoil C change are numerous and include changes in: vertical root distribution; recalcitrance of root material by alterations of its chemical composition; translocation of dissolved organic carbon (DOC) to subsoil horizons by water percolation; soil microbial processing of SOC; and soil fauna activities that can transfer SOC to deeper horizons (Lorenz and Lal, 2005). Size fractionation of SOC into particulate organic carbon (53-2000 μm; POC) and fine C (<53 μm) offers a relatively simple methodology for identifying which of the above-mentioned mechanisms are active in both surficial and subsoil SOC change. If DOC was contributing to increased SOC storage with depth, this would have to be recovered as the fine fraction in a SOC size fractionation. Alternatively, if a change in root residue quantity or quality was occurring under different land uses, then this should be recovered mostly as an increase in subsoil POC.

Particulate Organic Carbon (POC)

Many studies have identified POC as the most susceptible pool of SOC to cultivation induced losses and as sensitive to land management (Cambardella and Elliott, 1992; Causarano et al., 2008; Chan, 2001; Franzluebbers and Arshad, 1997; Skjemstad et al., 2006; Tiessen and Stewart, 1983; Wander et al., 1994). A review of light-fraction SOM obtained by dense liquid fractionation and POC obtained by size fractionation found that POC makes up a median value of 27.0% of total soil C in forest soils (range of 10.0-48.4%, 13 studies) and an average of 19.0% in agricultural soils (range of 1.6-65.1%, 65 studies) (Gregorich et al., 2006). Breaking down the agricultural studies into those that compared CT and NT systems showed no difference in the proportion of total C as POC (20.4% and 19.8% of total-C, respectively). A clear difference in POC quality emerged from their meta-review as C/N ratios were 15.5 and 33.7 for the agricultural and forest soils, respectively. They also showed a clear relationship between the fraction size obtained and the C/N ratio (y=0.0026(x) + 12.21, y=C/N ratio, and x=log(mid-point of the fraction size in μm), r^2=0.76). These results lend support for the functional relevance of the POC fraction, where SOC of decreasing size typically represents older fractions in a state of increasing decomposition evident in the narrowing C/N ratio. However, uncertainty exists as to whether POC is lost due to changes in biochemical resistance of the residues to decomposition or due to loss of physical protection from decomposition through alteration of soil structure.

Physical Protection: Aggregates

Since physical protection of SOC within stable soil aggregates is considered to be one of the major SOC stabilization mechanisms, (Mikutta et al., 2006; Six et al., 2002a; von Lutzow et al., 2006), the effects of land management on aggregate stability are accepted as key factors in determining SOC levels (Six et al., 1998). Although criticism of soil aggregate-focused research has argued that researchers are giving too little attention to the regulatory role of soil porosity (Young et al., 2001), there is substantial evidence that aggregates have boundaries with ecological significance, elucidated with a variety of methods under a range of conditions (Golchin et al., 1994; Hassink et al., 1993; Jasinska et al., 2006; Rasmussen et al., 2005; Vreeken-Buijs et al., 1998).

Structural protection mechanisms are generally envisioned to operate through pore size exclusion of extracellular enzymes, microbes, and soil micro-fauna, in addition to pore-mediated regulation of the environmental factors that control microbial activity, such as oxygen concentration, temperature, and water content. The key concept is that intra-aggregate pores are finer (and perhaps more tortuous) than inter-aggregate pores, that is, the larger pores surrounding aggregates (Horn et al., 1994), so that decomposition is slowed within aggregates. The abundant research on the relationship between soil aggregation and SOC stabilization has produced several contrasting models of how physical protection of SOC occurs.

The classic aggregate hierarchy model suggests that soil structure arises from the binding of fine mineral particles into microaggregates (53 µm to 250 µm) eventually into macroaggregates (>250 µm) with increasing dependence on greater and more transient organic binding agents as the scale increases (Tisdall and Oades, 1982). In soils demonstrating an aggregate hierarchy, SOC concentration should increase with increasing aggregate size, as fine mineral particles absorb carbon and combine to form microaggregates and microaggregates further incorporate SOC binding agents to combine into water-stable macroaggregates. Subsequent studies attributed the loss of SOC in cultivated soils to exposure and to microbial attack of the SOC responsible for binding microaggregates into macroaggregates (Elliott, 1986). Oades (1984) modified the aggregate hierarchy theory and hypothesized that microaggregates formed around particulate organic C (POC, 53-2000 µm) enmeshed within macroaggregates. Following this modification, recent work in no-till and afforested systems suggest that decreased macroaggregate turnover in soils lacking mechanical disturbance is thought to result in higher rates of microaggregate formation and stabilization of fine POC (53-250 µm) within these microaggregates (Six et al., 2000a; Six et al., 2002b), not an increase in the organic binding agents that hold macroaggregates together. Following this line of thinking, loss of SOC in cultivated soils is explained by shorter macroaggregate turnover times and a reduced opportunity for formation of microaggregates around a fine POC core.

More recently, it has been hypothesized that increased pore connectivity in soils that are not tilled allows greater movement of dissolved organic carbon (DOC) from larger pores surrounding aggregates into intra-aggregate pore spaces, a flux which may be enhanced by wetting-drying cycles (Smucker et al., 2007). In tilled soils, disruption of the pore network effectively isolates substantial portions of the intra-aggregate pore space from replenishment of DOC either from root exudates, decomposition of POC, or litter leachate laden with DOC. Smucker et al. (2007) argue that proper management has the potential to "double or triple soil carbon levels" if these mechanisms are fully understood. The focus on DOC by Smucker et al. (2007) is in opposition to other work that has identified POC as the fraction of SOC most susceptible to management and soil structural disruption (Cambardella and Elliott, 1992; Causarano et al., 2008; Chan, 2001; Franzluebbers and Arshad, 1997; Skjemstad et al., 2006; Tiessen and Stewart, 1983; Wander et al., 1994). Size fractionation of SOC also offers a relatively simple way to address the difference in the proposed mechanisms put forth by Six et al. (2002b) and Smucker et al. (2007). If micro-scale fluxes of DOC is important to attaining maximum soil C storage capacity, then this should at least be recovered as fine C (<53 µm) in systems where significantly higher levels of SOC have been attained.

Soil acidification

Since the onset of the industrial revolution, combustion of fossil fuels has increased atmospheric concentration of sulfuric and nitric acids (Galloway, 2001). In addition, modern cropping regimes that use ammonium based fertilizers and legumes to boost soil N have also increased rates of nitrification and nitrate salt leaching (Moody and Aitken, 1997; Ridley et al., 1990). These enhanced, anthropogenic factors of soil acidification have led to concern over effects on water quality (Burns et al., 1981), forest productivity (Likens et al., 1996), and soil productivity in pastures and croplands around the world (Juo et al., 1995; Noble et al., 2002).

Soil acidification, defined as either a decrease in soil pH or a reduction in base saturation of the exchange complex, is a natural process necessary for crustal weathering to occur and for the production of soil bodies from rock. There are five major natural soil acidification processes: soil respiration and the concomitant generation of carbonic acid; the production of organic acids from microbial and root biochemistries; nitrification of ammonium to produce nitric acid; oxidation of sulfides in primary minerals and of organic sulfur in soil organic matter to produce sulfuric acid; and a preferential uptake of base cations over anions by plants (Binkley and Richter, 1987; Richter and Markewitz, 2001). How land use affects these processes of soil acidification is important to understanding the effects of management on long-term soil productivity.

Soil acidification is of special concern in areas with highly weathered soils that have low cation exchange capacity and inherently low levels of base cations. For instance, many eastern US forest soils are poorly buffered against enhanced soil acidification processes, especially loss of base cations through leaching and biomass harvesting (Federer et al., 1989). A reduction of soil pH in soils with considerable variable charge oxides can induce a loss of effective cation exchange capacity (ECEC) (Qafoku et al., 2000), an important component of soil fertility. A soil alkalinization and increase in ECEC was observed following conversion of native Costa Rican forests to pastures (Krishnaswamy and Richter, 2002), probably due to transfer of base cations balanced by carbonates in ash and balanced by organic anions in forest biomass. Similar observations were reported for grassland to forest conversion in South America (Farley et al., 2008). The authors found that export of cations through tree biomass in South American plantations had substantially reduced exchangeable cation pools compared to adjacent grassland soils, resulting in stream acidification as percolating water now made contact with a soil matrix of lower base saturation. Although leaching of base cations under the grassland was greater due to higher base saturation, the flux of base cations through tree biomass removal was of a much greater magnitude than stream exports draining grasslands (Farley et al., 2008).

Increases in soil acidity as a result of afforestation have been documented for reforestation of agricultural land around the world, including the southern US piedmont (Richter and Markewitz, 2001), southeastern US coastal plain (Markewitz et al., 2002), the northeastern United States (Driscoll and Likens, 1982), and Europe (Alriksson and Olsson, 1995; Ritter et al., 2003). Work on the mechanisms of soil acidification in areas of afforestation has suggested that internal ecosystem function is as important as acidic deposition in affecting soil change. A comparison of whole-tree harvesting versus leaching showed that for the majority of the sites plant uptake and removal would have a greater effect on limiting nutrient cations than leaching (Johnson et al., 1988). A proton budget approach suggested that after 34 years of *Pinus taeda* growth on an Ultisol, 44% of the acidification was due to base cation uptake by vegetation, 15% due to production of carbonic acid from soil respiration, and the remaining 41% was attributed to acidic deposition and associated leaching (Markewitz et al., 1998).

In contrast to these reports of soil acidification following afforestation, no reduction of exchangeable soil Ca^{2+} was evident fifteen years after a whole-tree harvest followed by forest re-growth, even though vegetation uptake by itself could have reduced exchangeable Ca^{2+} by 40% (Johnson and Todd, 1998). The authors speculated that either the exchangeable pool had been replenished via the non-exchangeable pool or that roots in the aggrading forest had accessed deeper soil pools of Ca^{2+} to meet its nutrient demands (soils were sampled to 45 cm). Similarly, high rates of nitrification and associated base cation leaching appeared to be buffered by non-exchangeable mineral pools in the western United States under Red Alder (Homann et al., 1992). Recent work in the northeastern United States has illustrated that mechanisms of soil acidification are still poorly understood (Bailey et al., 2005). In this work, the researchers identified large declines in exchangeable Ca^{2+} pools at two of four studied forested sites that had been sampled thirty years earlier. Assuming typical hardwood Ca^{2+} concentrations, the authors concluded that forest uptake could not account for the soil change at the sites with the highest loss, implying that leaching was responsible. In criticism that followed this work, it was estimated that leaching rates of Ca^{2+} at these sites would have had to have been 6.1 to 19 $kmol_c$ ha^{-1} yr^{-1} to account for the change, rates much greater than estimated annual deposition of SO_4^{2-} and N in that part of the world or previously observed Ca leaching rates (0.5-2 $kmol_c$ ha^{-1} yr^{-1}) (Johnson, 2005).

In order to predict the long-term effects of "acid rain" and land management, much effort has gone to developing models that predict the effects of acidification mechanisms on soil and water chemistry (Cosby et al., 2001; Reuss and Johnson, 1986; Verburg and Johnson, 2001). The basis of these models is the law of charge balance, which states that total cation charge must always equal total anion charge for a solution in equilibrium, and how it interacts with the soil exchange complex. Employing this conceptual model, the export of cations is expected to increase whenever the concentration of anions in solution is increased. The rate of base cation leaching (Ca^{2+}, Mg^{2+}, K^+, and Na^+) will be greatest in soils with high base saturation of the exchange complex whereas acidification of lakes and rivers, that is, transfer of acidic cations (H^+ and Al^{3+}) to surface waters via soil leaching, is expected to be greatest in soils with low base saturation. In this work, generation of HCO_3^- from dissolved CO_2, production of NO_3^- from nitrification, and production of organic acids by microbes and plants are given special attention, since they are expected to be the most land-use dependent of the dominant anions in natural soil waters.

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CHAPTER III

SOIL CARBON CHANGE THROUGH TWO METERS DURING FOREST SUCCESSION ALONGSIDE A 30-YR AGROECOSYSTEM EXPERIMENT[1]

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Abstract

While forest succession (FS) and no-till (NT) agriculture are generally assumed to have a beneficial effect on surficial soil organic C (SOC) stocks compared to conventional tillage (CT) management, land-use effects to depths >30 cm remain uncertain. This research compared SOC contents and composition to 2 m under CT, NT, and FS at the 30-yr Horseshoe Bend agroecosystem experiment in Athens, Georgia, USA. Soils from 0-2 m were fractionated into particulate organic C (POC, 53-2000 μm) and fine-C (<53 μm) fractions and bulk soil $\delta^{13}C$ signatures were determined. Soils from 0-28 cm were dry and wet sieved to estimate aggregate stability. Soil solutions were also collected at 0, 15, and 100 cm for dissolved organic C (DOC) analysis. Full-profile (0-2 m) SOC storage is 52 Mg ha^{-1} in CT, 60 Mg ha^{-1} in NT, and 62 Mg ha^{-1} in FS. Significant differences are limited to 0-5 cm and linked to enhanced aggregate stability under NT and FS. SOC storage under CT through vertical redistribution by inversion tillage is no longer apparent and has not compensated for the loss of SOC protection afforded by enhanced aggregate stability under NT and FS. Return of annual crop biomass to the agroecosystem soil has also not increased SOC stocks relative to FS, which also had a large accumulation of C in forest biomass. Increases in subsoil POC under FS and changes in soil $\delta^{13}C$ and C/N indicate that substantial subsoil C cycling has occurred. DOC fluxes at 0 cm were significantly greater under NT (200 kg ha^{-1} yr^{-1}) and FS (210 kg ha^{-1} yr^{-1}) compared to CT (80 kg ha^{-1} yr^{-1}). DOC fluxes at 15 cm are estimated to be 20 kg ha^{-1} yr^{-1} under CT and NT and 40 kg ha^{-1} yr^{-1} under FS. At 100 cm, DOC fluxes are 2 kg ha^{-1} yr^{-1}, regardless of land use. An increase in FS POC of 2 Mg ha^{-1} from 15-100 cm outweighs cumulative differences in DOC input to this layer, implicating deep forest rooting and bioturbation as more active mechanisms in subsoil C change.

Introduction

Soil organic carbon (SOC) represents an important global pool of C. There is an estimated 1500 Pg of SOC globally (Lal, 2004). SOC is a component of soil organic matter (SOM), which is not only a storehouse for C but a critical soil fraction that functions as: (1) the primary soil medium through which N is stored and made available to plants; (2) a soil particle binding agent that affects soil erosion, water infiltration and water holding capacity; and (3) a pH dependent, chemically active surface that enhances cation exchange capacity, as well as the retention of organic and metallic contaminants. So, while much recent research emphasizes the role of SOC in carbon sequestration, there is an implicit acknowledgement that SOM is involved more broadly in ecosystem function.

Long-term experiments that monitor changes in levels of SOC in relation to land treatments are valuable tools for understanding how management decisions will influence future soil fertility and SOC storage (Paul et al., 1997). One such study regarding tillage effects on SOC concentrations is the Horseshoe Bend (HSB) agroecosystem experiment in Athens, Georgia, USA (Figure 3.1). An analysis of SOC data from 1982-1991 at this site concluded that while the no-till (NT) system maintained significantly higher SOC concentrations in the upper 5 cm, SOC concentrations were found to be slightly higher from 5-21 cm under conventional tillage (CT) due to vertical redistribution (Hendrix 1997). Therefore, there was a non-significant difference in SOC content of 4 Mg C ha^{-1} from 0-21 cm. Interestingly, a net loss occurred in both systems from 1982 to 1991: a 25% loss in CT (9 mg C ha^{-1}) and a 15% loss in NT (5 Mg C ha^{-1}).

In light of the recent controversy concerning whether no-till systems truly store more SOC compared to conventional tillage systems when a deeper soil profile is considered (Blanco-

Canqui and Lal, 2008; Carter, 2005), a re-evaluation of SOC storage at the HSB agroecosystem experiment on a deeper profile basis is warranted. Also of interest is the fact that the majority of the landscape at HSB is dominated by secondary forest (Figure 3.2). Given the global interest in SOC change in relation to a broader set of land uses (Guo and Gifford, 2002) and the above-mentioned loss of SOC in the HSB agroecosystem during the first decade of the experiment, there was also interest in examining how adjacent soils undergoing forest succession have responded during the same time period at HSB. A recent review comparing NT and CT management clearly demonstrated the benefits of NT systems on carbon contents from 0-10 cm (West and Post, 2002). In a second review, however, comparing no-till to full-inversion tillage (i.e. moldboard plowing), SOC concentrations were higher just below the plow layer in many of the CT systems, which was attributed to repeated transfer of surficial crop residues to the depth of soil inversion (Angers and Eriksen-Hamel, 2008). Nevertheless, for soils sampled to ≥ 30 cm in their review, NT soils still showed a small, but significant (p=0.03) net increase of 4.9 Mg C ha^{-1} (100.3 vs. 95.4 Mg C ha^{-1}). Yet another review of SOC found that concentrations can change significantly to a depth of 100 cm, but that deeper changes depended upon a number of factors, notably the type of land use conversion, vegetation, and climate (Guo and Gifford, 2002).

Subsoil C is not inherently recalcitrant; its protection may be linked to physical occlusion in large peds that turn over slowly compared to A horizon structural units which experience more frequent bioturbation in unmanaged systems (Ewing et al., 2006). Mechanisms of potential subsoil C change are numerous and include changes in: vertical root distribution; recalcitrance of root material; translocation of dissolved organic C (DOC) to subsoil horizons by water percolation; soil microbial processing of SOC; and soil fauna activities that can transfer SOC to deeper horizons (Lorenz and Lal, 2005). Size fractionation of SOC into particulate organic carbon (53-2000 μm; POC) and fine C (<53 μm) may offer a relatively simple methodology for identifying which of the above-mentioned mechanisms are active in both surficial and subsoil SOC change. If DOC was contributing to increased SOC storage with depth, this would have to be recovered as the fine fraction in a SOC size fractionation. Alternatively, if a change in root residue quantity or quality was occurring under different land uses, then this should be recovered mostly as an increase in subsoil POC.

Many studies have identified POC as the most susceptible pool of SOC to cultivation induced losses (Cambardella and Elliott, 1992; Causarano et al., 2008; Chan, 2001; Franzluebbers and Arshad, 1997; Skjemstad et al., 2006; Tiessen and Stewart, 1983; Wander et al., 1994). However, uncertainty exists as to whether POC is lost due to changes in biochemical resistance of the residues to decomposition or due to loss of physical protection to decomposition through alteration of soil structure.

Structural protection mechanisms essentially operate due to pore size exclusion of extracellular enzymes, microbes, and soil micro-fauna, as well as regulation of the environmental factors that control microbial activity, such as oxygen concentration and water content. The key concept here is that intra-aggregate pores are finer (and perhaps more tortuous) than inter-aggregate pores, that is, the larger pores surrounding aggregates (Horn et al., 1994), so that decomposition is affected within aggregates because of differences in porosity. Although recent criticism of aggregate-focused work has argued that researchers are giving too little attention to the regulatory role of soil porosity (Young et al., 2001), there is substantial evidence that aggregates have boundaries with ecological significance, elucidated with a variety of methods under a range of conditions (Golchin et al., 1994; Hassink et al., 1993; Jasinska et al., 2006; Rasmussen et al., 2005; Vreeken-Buijs et al., 1998).

The aggregate hierarchy model explains that soil structure arises from fine mineral particles to microaggregates (53 μm to 250 μm) to macroaggregates (>250 μm) with increasing dependence on greater and more transient organic binding agents as the scale increases (Tisdall and Oades, 1982). This model explains loss of SOC in cultivated soils by exposure to microbial attack of the organic glues responsible for binding microaggregates into macroaggregates upon disruption of aggregates by tillage (Elliott, 1986). A modification of the theory explains that decreased macroaggregate turnover in soils not exposed to mechanical disturbance is thought to result in higher rates of microaggregate formation and SOC stabilization (primarily POC) within these microaggregates (Oades, 1984; Six et al., 2000a). A more recent theoretical addition to the relationship between soil structure and carbon storage explains that soils with pore networks that are frequently disrupted by tillage have large portions of the soil matrix isolated from replenishment of soil carbon through diffusion of DOC into inaccessible micropores (Smucker et al., 2007). Again, size fractionation of SOC should help in evaluating this as a potential mechanism of SOC change.

The overall objective of this work is to examine the carbon content and composition from a full profile (0-2 m) perspective under conventional tillage, no-till, and forest succession. Three questions are addressed: (1) Has SOC increased in NT and FS relative to CT? (2) Is soil aggregate stability linked to any observed changes in SOC, particularly at depths not previously studied at HSB? (3) What role could DOC play in surficial and subsoil SOC changes?

Methods

Site Description

The Horseshoe Bend (HSB) agroecosystem experiment (33° 57’ N, 83° 23’W) is a long-term comparison of conventional and no-tillage treatments begun in 1978. Based on a series of aerial photos, HSB had been cleared entirely of trees except for a narrow strip along the Oconee River at least since 1938 (Figure 3.2). The site was mostly used for pasture and forage production by the University of Georgia (UGA) Dairy until 1965 when the Institute of Ecology at UGA acquired HSB for research (Hendrix, 1997). The area underwent natural succession in 1966 except for the future agroecosystem site, which was tilled to plant a crop of millet for a separate, earlier study (Barrett, 1968). Afterwards, the site went fallow and was used for a prescribed burn study and a N fertilization study (Bakelaar and Odum, 1978; Odum et al., 1973). In 1978, the study area was divided into equal numbers of conventional and no-till 0.1 ha plots, and the old-field vegetation was mowed (Hendrix, 1997). Since the experimental plots were in fallow from 1966, the current no-till plots have not been tilled for forty-two years. Conventional tillage has been performed twice annually in most years with moldboard plowing to a depth of 15 cm, followed by disking. In 1981, each agricultural plot was split into different winter crop treatments with winter rye (*Secale cereale*) grown on half of each plot and N-fixing crimson clover (*Trifolium incarnatum*) grown on the other half until 1984 and then again from 1989 to the present (Coleman et al., in press; Hendrix, 1997). From 1978-1998, summer crops have included sorghum (*Sorghum bicolor*), soybeans (*Glycine max*), corn (*Zea mays*), and kenaf (*Hibiscus cannabinus*). Since 1999, a second split-plot has been assigned to the agroecosystem experiment for a comparison between summer crops of non-Bt and Bt-cotton (*Gossypium hirsutum* L.) (Coleman et al., 2006). Soil sampling in the current study sought to estimate an average effect of no-tillage and conventional tillage on the measured properties by sampling equally among the winter cover split-plots before compositing; the effects of transgenic cotton on soil C and N were considered negligible, since earlier work showed no difference in decomposition rates between non-Bt and Bt-cotton residues (Lachnicht et al., 2004).

Three secondary, hardwood forest plots adjacent to the tillage experiment and a fourth afforested plot approximately 80 m to the west of the experiment were established in 2007 (Figure 3.2). These areas were intended to represent a third treatment, referred to henceforth as forest succession. All plots were on the same alluvial terrace as the agroecosystem plots and observed to be part of the same cleared area in the aerial photograph (Figure 3.2). Most likely, these afforested plots were not tilled in 1966, which means they essentially underwent a pasture to forest conversion. The soils under all three land uses have been re-classified from a clayey, kaolinitic, thermic, Rhodic Kanhapludult (Beare et al., 1997) to a fine-loamy, kaolinitic, thermic, Typic Kanhapludalf based on new particle-size analysis data in the control section and measurements of base saturation that are >98% in all three treatments at 140 cm (i.e., 125 cm below the top of the kandic horizon).

Aboveground Forest Biomass: C contents

In July 2008, individual trees were measured for total height and diameter at breast height (dbh) and identified by species. Total aboveground tree biomass (above-stump wood, bark, and foliage) was estimated from allometric equations for pignut hickory (*Carya glabra*), elm (*Ulmus spp.*), water oak (*Quercus nigra*), sweet gum (*Liquidambar styraciflua*), yellow poplar (*Liriodendron tulipifera*), green ash (*Fraxinus pennsylvanica*), and black locust (*Robinia pseudoacacia*), using both height and dbh information (Clark and Schroeder, 1986; Clark et al., 1985; Clark et al., 1986a). These species accounted for 90% of the total biomass. The remaining tree species were grouped by hard-hardwood and soft-hardwood species with aboveground biomass estimated using corresponding allometric equations for these groups (Clark et al., 1986b). Tree C contents were assumed to be 50% of the biomass estimates.

Soil Sampling and analysis

In March 2007, soil profiles were sampled in each of the twelve HSB experimental plots (n=4 per treatment) in seven depth classes: 0-5, 5-15, 15-30, 30-50, 50-100, 100-150, and 150-200 cm. To sample the 0-50 cm depth classes, a 2.2 cm diameter slide hammer coring device was used to obtain five cores from each plot: two cores from each split-plot of rye and clover and one core on the border between the split-plots. In the agroecosystem plots, one hole was augered in the center of each plot on the split-plot border between the clover and rye crops to sample the 50-100, 100-150, and 150-200 cm depth classes. Two holes were augered in each forested plot and were composited by depth class. These samples were air-dried, crushed with a rolling pin, and then passed through a 2 mm sieve to remove coarse material. Separate bulk density samples were collected in September 2008. Two 7.5 cm diameter by 5 cm depth cores per plot were collected for the 0-5 cm depth class (n=24). Two additional 7.5 cm diameter by 7.5 cm height cores were collected within the 5-15 cm (i.e., 6-13.5 cm) depth (n=24). In the 15-30 cm layer one core per plot from 19-26.5 cm (n=12) was obtained. For 30-50 and 50-100 cm, in half of the plots for each land use, one core was collected from 36-43.5 cm and another from 71-78.5 cm (n=6 per depth class).

Soil sub-samples were pulverized in a Spex 8200 ball-mill grinder and total C and N was determined using dry combustion on a CE Elantech NC 1110 analyzer (Lakewood, NJ). Earlier mineralogical work on subsamples showed no evidence of carbonates so no pre-treatments were performed (Devine, unpublished data, 2008). $\delta^{13}C$ signatures were determined by continuous-flow isotope-ratio mass spectrometry using a Thermo-Finnigan Delta V Isotope Ratio Mass Spectrometer (Bremen, Germany) coupled to a Carlo Erba CHN Combustion Analyzer via Thermo-Finnigan Conflo III Interface (Milan, Italy). $\delta^{13}C$ signatures are presented as the relative difference between the sample and Pee Dee Belemnite (PDB) in parts per thousand, such that $\delta^{13}C‰ = (R_{sample}/R_{PDB} - 1)*1000$, where R is $^{13}C/^{12}C$. To obtain particulate organic C (POC) and fine-C fractions, a 5 g subsample was dispersed using 25 mL of 0.5% Na-hexametaphosphate (HMP) by shaking for 16 h. The resulting soil slurry was washed through a 53 μm sieve using 0.5 L of DI water to fractionate the soil into: (1) >53 μm (POC) and (2) <53 μm (fine-C). A rubber policeman was used to aid in dispersion of stable soil aggregates in the 0-5 and 5-15 cm depth classes when necessary. Fine-C and POC fractions were also pulverized and C and N determined. A mass correction was made for the amount of Na-HMP recovered in the fine fraction prior to estimation of fine-C and N concentrations.

In order to quantify aggregate stability, separate samples were obtained at the end of the summer growing season in October 2007 using a 5 cm diameter corer attached to a slide-hammer to a depth of 28 cm. Each core was divided into 0-5, 5-15, and 15-28 cm and passed through a 10 mm mesh by gently breaking the cores along planes of weakness before air-drying. These samples were dry-sieved through 6.3, 4, 2, and 1 mm screens to obtain dry aggregate size classes. A separate subsample of the < 1 mm dry aggregates was sieved on a 0.25 mm screen. Sub-samples of 50 g were then weighed out by re-combining all the dry aggregate size classes according to their proportional mass for a whole sample. This ensured that each sub-sample accurately represented the whole-soil dry aggregate size distribution for a whole sample. This has been acknowledged as a methodological issue in determining aggregate size distributions (Kemper and Chepil, 1965). These 50 g sub-samples were then wet-sieved with a modified Yoder (1936) apparatus that is made to process larger masses of soil on nested sieves (21.6 cm) and to permit complete recovery of all soil from each sample. The method obtains four aggregate size classes: (i) > 2 mm; (ii) 0.25 - 2 mm; (iii) 0.053-0.25 mm; and (iv) <0.053 mm. Wet aggregate mean-weight diameters (MWD) were calculated by multiplying the proportion of soil in each of these four aggregate size classes by the mid-point of the size class. The calculation of the dry MWD used the same size divisions as the Wet MWD except no <0.053 mm fraction was included, since dry sieving material through a 0.053 mm sieve is not practical. The aggregate stability index was then calculated by dividing the Wet MWD by the Dry MWD; an index of 1 represents perfect structural stability.

Solution Sampling and analysis

Wet-fall, litter leachate and soil solutions were collected every 7-10 days. One automated, battery-powered dry fall-wet fall collector (Aerochemetrics Bushnell, FL) was placed in the middle of the agroecosystem experiment to collect wet-fall precipitation. Three bulk precipitation collectors were also placed in open areas but persistent bird-dropping contamination invalidated chemical concentrations, although volumes were utilized. Litter leachate was collected with PVC pipes and matching end-caps that were cut into thirds and fashioned into 9 cm x 30 cm troughs connected by polypropylene tubing to a 4 L bottle stored in a hole. Pieces of aluminum flashing were used as covers for the holes to protect litter leachate solution from direct sunlight. The thin O-horizons (<1 cm) under each PVC trough in forest succession and no-till plots were cut before installation and placed into the collector. For the CT and NT plots, one collector was installed in a rye split-plot and the other in a clover split-plot. Each litter leachate sample was analyzed separately with plot sub-samples averaged together before statistical analysis. To collect soil solution, two Prenart Super Quartz tension lysimeters (Prenart Equipment Aps, Frederiksberg, Denmark) connected to 2 L Nalgene bottles were installed in each plot: one at 15 cm depth and the other at 100 cm depth. Lysimeters were divided evenly between clover and rye split-plots for the CT and NT treatments. A 90° PVC triangle was used to guide an auger into the ground at a 45° angle to avoid disturbing the soil profile directly above the lysimeter. A punch tube with the same diameter as the lysimeters was used to make the final hole where the lysimeters were installed at the bottom of the augered hole. A slurry of acid-washed silica flour was also used around each lysimeter to ensure good contact with the soil matrix. The holes were back-filled with soil carefully returned in the same order as it was removed. When soil moisture was sufficient for collection, tensions of -0.065 to -0.075 MPa were established twice each week in each lysimeter-bottle combination with a hand vacuum pump.

All samples were collected on the same day, filtered through Whatman 0.45 µm polycarbonate filters, and refrigerated until analysis. Analyses included total dissolved nitrogen (TDN) and non-purgable organic carbon (NPOC) after acidification to pH 2 and sparging with CO_2-free air for 3 minutes (Shimadzu TOC 5000, Columbia, Maryland, USA). Analysis for NO_3^- and NH_4^+ was on a Dionex DX 500 Ion Chromatograph (Dionex, Sunnyvale, CA). TDN and NPOC were analyzed from Aug 2007 to 2008 while NO_3^- and NH_4^+ analysis only extended from Nov 2007 to Aug 2008. Dissolved organic N (DON) was estimated as:

$$DON = TDN - (NH_4^+\text{-}N + NO_3^-\text{-}N)$$

Hydrologic Fluxes

The goal of estimating hydrologic fluxes was not to separate treatment effects on water flow through the soil but to scale concentration data from lysimeters to a field-scale flux. Fluxes were modeled from 1978 to 2008. Details of the model are in Devine (2009: Appendix A). In brief, to estimate hydrologic flux a one-dimensional model was created in HYDRUS (2D/3D) version 1.02 (Simunek et al., 2007). The 1 m model profile was divided into five layers to match the soil depth classes described previously, which were separated into distinct 1 cm vertical increments. Soil hydraulic parameters (θ_r, θ_s, α, n, and K_s) for each layer were estimated using the Rosetta Lite v.1.1 tool that accompanies HYDRUS (2D/3D) (Vangenuchten, 1980). Potential evapotranspiration (PET) based on the Penman-Monteith method was estimated using ETo Calculator (Raes and Munoz, 2008). A second estimate of PET was made using the Thornthwaite method (Thornthwaite, 1948). All climactic data were either from the Athens Ben Epps Airport (33°57' N, 83°20' W) available through the National Climactic Data Center (NCDC, 2007) or from preliminary data available through the National Weather Service (NWS, 2008). Generation of an internal mesh-line available in HYDRUS (2D/3D) at 15 cm depth allowed for estimation of a water flux at 15 cm (Simunek et al., 2007). HYDRUS (2D/3D) automatically generates an output file for the free drainage boundary in the model, which allowed for estimation of the water flux at 100 cm depth. Since no quantitative data were available to either calibrate or verify the model, modeled soil tensions at both 15 and 100 cm were graphed to assure periods of low and high tension matched periods of lysimeter collections in the field.

Statistical Analysis

Differences in 0-2 m contents of total SOC, POC, fine-C, and profile C:N were tested with a one-way ANOVA with land use as the main effect (n=4). The same analysis was performed for a sum of 15-100 cm contents to aid in interpretation of lysimeter data (n=4). Treatment effects were also evaluated for C:N ratios and δ^{13}C signatures in addition to the above components by performing the same ANOVA for each of the seven depth classes (n=4). For each measured component in the water samples, annual volume-weighted mean lysimeter concentrations and litter leachate fluxes were similarly evaluated (n=4). Post-hoc tests were performed in all cases using the LSMEANS statement in PROC GLM to evaluate the significance of mean separations with p-values adjusted by Tukey's honestly significant difference (α=0.1).

Results

Aboveground Forest Biomass

Aboveground forest biomass at HSB, which includes tree wood, bark, and foliage, is estimated at 419 ± 89 Mg ha^{-1} or 209 ± 44 Mg C ha^{-1} (mean ± 1 SD). Since forest succession began in 1966, this is a mean annual biomass accumulation of 10.0 Mg ha^{-1} yr^{-1}.

Soil organic C concentration and composition

Both the NT and FS profiles have significantly greater soil organic C (SOC) contents than the CT profile (p=0.08 and p=0.04, respectively) (Table 3.1). By depth class, however, the only significant differences in terms of SOC and fine-C concentrations occur in the shallowest soil depth (0-5 cm) (Table 3.2; Figures 3.3 and 3.4). For SOC from 0-5 cm, FS had a higher concentration than NT ($p=0.02$), which had a higher concentration than CT ($p<0.001$). For fine-C from 0-5 cm, FS and NT both have significantly higher concentrations than CT ($p<0.001$). SOC content differences in the 0-5 cm layer accounts for 56% of the 0-2 m mean content difference between FS and CT and 66% of the 0-2 m content difference between NT and CT. The remaining 44% of the 0-2 m content difference between FS and CT can be accounted for in mean content differences between 15 and 100 cm, which is statistically insignificant when analyzed separately ($p=0.18$) (Table 3.1). For NT and CT, the remaining 34% content difference is explained by differences extending to 2 m, which is also statistically insignificant when analyzed separately ($p=0.41$: comparing 15-200 cm soil C contents) (Table 3.2).

Mean POC concentrations under FS are consistently higher through 2 m (Figure 3.4; Table 3.2). The FS soil profile has significantly greater contents of POC than both the NT ($p=0.001$) and CT ($p<0.0001$) profiles (Table 3.1). The NT soil profile POC contents are also greater than the CT profile ($p=0.07$). POC accounts for 23% of the 0-2 m SOC content under FS compared to 14% under CT and 16% under NT (Table 3.1). In contrast to SOC, when POC contents are summed from 15-100 cm, the FS-CT comparison is significant ($p=0.06$), though the FS-NT comparison is not ($p=0.22$) (Table 3.1). POC accounts for 70% of the 0-2 m SOC content difference between CT and FS but only 30% of the 0-2 m SOC content difference between CT and NT.

The $\delta^{13}C$ isotopic signatures clearly diverge between the FS and agroecosystem soil profiles to a depth of 1 m (Figure 3.3). The FS $\delta^{13}C$ signature is significantly more depleted in all depth classes to 1 m relative to NT and CT except for a comparison with NT from 15-30 cm (Table 3.3).

The whole profile C:N ratio is significantly elevated under FS compared to CT and NT (Table 3.1). The FS soil C:N ratio is significantly higher for each depth increment from 0-100 cm with the exception of the 15-30 cm depth class compared to CT ($p<0.1$ for all contrasts) but only significantly higher from 0-5 cm compared to NT ($p<0.0001$) (Figure 3.5; Table 3.3). Significant differences among the land uses for fine-C:fine-N and POC:PON ratios did not extend as deep (Table 3.3), though the POC:PON and fine-C:fine-N ratios do show a wide divergence and suggest a difference in degree of decomposition (Figure 3.5). The FS and CT POC:PON ratios were significantly higher from 0-5 cm compared to NT ($p<0.02$) (Table 3.3). The FS POC:PON ratio was also significantly higher from 0-5 and 15-30 cm compared to CT ($p<0.09$) (Table 3.3). Significant differences in the fine-C:fine-N were limited to 0-5 cm with FS significantly higher than both CT and NT ($p<0.001$) (Table 3.3). Finally, recovery of POC and fine-C relative to measurement of total SOC averaged 96.4% for 0-50 cm depth classes and 113.4% for the 50-200 cm depth classes.

Aggregate stability

Both the NT and FS soils are significantly more stable than the CT soil from 0-5 cm. FS is also more stable from 5-15 cm and 15-28 cm relative to the agroecosystem soils, and aggregate stability clearly declines with depth for all three treatments (Table 3.4).

Dissolved Organic Carbon concentration and composition

Both NT and FS litter leachate (LL) concentrations of DOC were generally higher than concentrations in the CT plots, since it lacks a litter layer (Figure 3.6). This results in a significantly lower DOC flux in CT LL (Table 3.5). Compared to LL, 15 cm soil solution DOC concentrations are about an order of magnitude less and were consistently higher under FS during the winter and spring (Figure 3.6), which is when most of the leaching occurs in the eastern United States. However, DOC flux comparisons between FS-CT and FS-NT are not significantly different at this depth (p=0.12 and 0.15, respectively; Table 3.5). At 1 m depth, DOC concentrations are not much higher than that in rainfall, which had an annual volume-weighted mean of 1.27 mg L^{-1}, and there was no separation of the annual volume-weighted mean concentrations among land uses.

Dissolved organic N (DON) LL fluxes were significantly higher under NT compared to CT (p=0.0004) and FS (p=0.07) (Table 3.5). The FS DON flux in LL was also significantly greater than the CT DON flux (p=0.01). DON accounted for approximately half of the total dissolved N (TDN) in LL under all three land uses from 26-Oct-07 to 1-Aug-08. There was a clear difference in the quality of dissolved organic matter (DOM) in LL under FS, as it had a significantly higher DOC:DON ratio for this same time period compared to CT and NT (p<0.0001 for both contrasts) (Table 3.5).

On average, DON was <20% of TDN for the agroecosystem plots at both soil depths (Table 3.5), while concentrations of DON were consistently elevated under FS compared to CT and NT at 15 cm but not 100 cm depth (Figure 3.7). In terms of DOM quality, differences were not as evident in soil solution as they were for LL. DOC:DON ratios at 15 cm depth by plot ranged from 13 to 47 with no significant differences among the treatments (Table 3.5). At 100 cm, the DOC:DON ratio under FS was significantly lower than NT (p=0.10) but not compared to CT (p=0.24) (Table 3.5). Only for the FS profile did DOC:DON ratios consistently decrease with depth from LL to 100 cm, suggesting greater decomposition with movement down the profile. Finally, these DOC:DON ratios for volume-weighted means by plot were greater than fine soil C:N ratios in all cases (Table 3.5; Figure 3.5).

Discussion

Full profile SOC change in relation to aboveground biomass accumulation

Three decades of divergent land uses have led to 20% greater soil organic C (SOC) content in the no-till (NT) and forest succession (FS) soil profiles relative to conventional tillage (CT) (Table 3.1). These differences are consistent with the average 30% carbon loss from tillage reported by Davidson and Ackerman (1993) but greater than the more recent review comparing deeper SOC content changes between NT and full-inversion CT (Angers and Eriksen-Hamel, 2008). The SOC change is small relative to the aboveground forest biomass accumulation of approximately 140-280 Mg C ha^{-1} (95% confidence interval). This large biomass accumulation must partly reflect the relatively fertile soils at HSB (Devine 2009) and possibly year-round water availability through tree root access of the local water table. The Oconee River surrounds three sides of the HSB plots and is only 4-6 m below the elevation of the alluvial terrace. On an alluvial soil in North Carolina, secondary forest succession measured over 50 yr supported initial productivity of 21 Mg biomass ha^{-1} yr^{-1} (annual litter fall + tree biomass accumulation) and eventually averaged 18.5 Mg biomass production ha^{-1} yr^{-1} (Peet, 1981). This is near the highest forest productivity reported for an eastern US forest: 24 Mg biomass ha^{-1} yr^{-1} for a *Liriodendron tulipifera* forest in the Smoky Mountains, North Carolina, USA, where mature cove forests are estimated to accumulate total biomass of 500-600 Mg ha^{-1} (Whittaker, 1966).

Given the current aboveground biomass estimate, mean annual increment over 42 years of forest growth at HSB is 10 Mg ha^{-1} yr^{-1}. While aboveground biomass has accumulated with

FS, substantial quantities of biomass have cycled in and out of the agroecosystem. From 1984 to 1990, aboveground biomass production averaged 15.7 Mg ha^{-1} yr^{-1} in NT and 13.0 Mg ha^{-1} yr^{-1} in CT (Hendrix, 1997). Since only small fractions of biomass have been removed for sampling, the incorporation of this biomass to the soil under CT has obviously not compensated for loss of SOC through disruption of soil structure. Nor has return of biomass to the surface in the NT system led to an increase in SOC compared to the FS profile. This may be related to differences in litter quality and decomposition rates between the agroecosystem and forest.

Mechanisms of SOC change

Overall, content differences from 0-5 cm account for 55 and 66% of the full profile content differences between CT-FS and CT-NT, respectively. Interestingly, differences in POC only account for 30% of the difference in 0-2 m SOC when comparing CT and NT whereas differences in POC account for 70% of the full-profile content difference between CT and FS. This suggests that the majority of SOC is not stabilized until it is highly processed, that is, it is < 53 μm in size under NT. Thus, micro-scale DOC fluxes in a better connected NT pore network could explain the majority of the difference in SOC contents between NT and CT but not the majority of the difference between FS and CT (Smucker et al., 2007).

The increase in SOC at the surface under FS and NT is linked to enhanced aggregate stability (Table 3.4) that may provide greater physical protection of SOC from decomposition. This mechanism has been evaluated in previous work comparing the NT and CT soils at HSB where destroying aggregates increased mineralization of protected SOC pools (Beare et al., 1994b). The slightly elevated level of POC from 5-15 cm under CT compared to NT is consistent with the review on inversion tillage where residues are preserved from decomposition at the bottom of the plow layer (Angers and Eriksen-Hamel, 2008), but is not sufficient to make up for the loss of carbon from 0-5 cm under CT. The FS soil was more stable from 5-28 cm compared to both NT and CT, which may be linked to significant increases in POC under FS from 5-15 cm. However, POC concentrations were not different from 15-28 cm between NT and FS, despite the greater aggregate stability under FS. This suggests that enhanced aggregate stability does not always lead to greater protection of SOC from decomposition.

Previous work at HSB also implicates not just physical but biological mechanisms in the stabilization of SOC and may explain why a greater proportion of the additional SOC under NT is stored in the fine fraction. Higher densities of earthworms were observed under no-till and forested conditions compared to CT over a three-year period (Hendrix et al., 1992). The two dominant species at HSB, *Aporrectodea caliginosa* (endogeic species) and *Lumbricus rubellus* (epigeic species) (Parmelee et al., 1990), have recently been implicated in positively affecting incorporation of SOC within aggregates (Bossuyt et al., 2005; Bossuyt et al., 2006). Thus, the observed differences near the surface may not simply be a result of the absence of tillage, but also due to enhanced earthworm activity that, while increasing aggregate turnover, enhances incorporation and stabilization of organic residues into aggregates. Indeed, POC:PON and whole soil C:N ratios from 0-5 cm are significantly higher under CT compared to NT, suggesting greater processing of residues followed by their stabilization near the surface in NT (Figure 3.5). The NT $\delta^{13}C$ signature is also significantly depleted from 0-5 cm compared to CT, implying greater incorporation of relatively depleted residues from C_3 crops grown in the agroecosystem since 1999 (Figure 3.3). Previous research at HSB, however, demonstrated $\delta^{13}C$ from individual NT aggregate size fractions in 1997 was already depleted relative to CT prior to the C_3 switch

(Arce Flores and Coleman, 2006). Thus, differences in SOC cycling before the C_3 switch may also explain the contrast in the present whole-soil isotopic signature between CT and NT.

Although differences in total SOC concentrations and contents are only clearly significant in the uppermost soil layer (0-5 cm) (Figure 3.3), this does not imply that no carbon cycling has occurred deeper in the soil profile. The $\delta^{13}C$ signature, size fractionation of SOC, and C:N ratios demonstrate that SOC is changing below depths commonly measured in land use change studies (Figures 3.3-3.5). Input of depleted ^{13}C material from C_3 bottomland hardwoods and relatively enriched ^{13}C material from C_4 summer crops grown in the CT and NT plots from 1978-1998 have led to distinctly different $\delta^{13}C$ signatures to a depth of 1 m.

Consistently higher concentrations of POC under the forest also occur to a depth of 2 m. Since POC accounts for a small proportion of the 0-2 m C (14-23% among the treatments), significant changes in this fraction from 15-100 cm under FS has not resulted in a statistically significant change in total SOC from 15-100 cm (Table 3.1). Significantly higher soil C:N ratios under FS compared to CT may reflect these new POC inputs that, when isolated, show a clearly higher C:N ratio compared to the fine fraction (Figure 3.5). Three possible mechanisms may explain these observed changes in subsoil POC concentrations and subsoil SOC quality: (1) subsoil root biomass and turnover is greater under forest succession, resulting in greater inputs of POC and an increase in the total soil C:N ratio (2) forest roots are more recalcitrant than crop roots, resulting in longer turnover times of POC (3) translocation of POC to subsoil by anecic earthworms may be greater under FS.

While overall earthworm populations were consistently higher under NT compared to FS during monitoring in the late 1980s (Hendrix et al., 1992), an exotic, anecic earthworm (*Lumbricus terrestris*) known to make vertically oriented burrows that connect the surface soil to the subsoil is common in the forest soil but rarely found in the agroecosystem (Callaham and Hendrix, 1997). This means that deep translocation of POC by earthworms could explain the subsoil POC increase under FS. Unfortunately, no data about either deep root production in the forest or differences in root litter quality between the forest and agroecosystem are available at HSB. Global reviews of root distributions and rooting depth by biome do show that temperate forests tend to root more deeply and have more root biomass than croplands or temperate grasslands (Canadell et al., 1996; Jackson et al., 1996). But the review by Jackson et al. (1996) found only nine studies that sampled roots quantitatively to a depth of at least 2 m.

Another unexpected result was that POC made up an increasing proportion of total soil C with increasing depth below 30 cm for all three land uses (Figure 3.4). Size fractionation of SOC has not previously been employed to these depths, though the conceptually similar density fractionation of SOC has been done to greater depths with contrasting results. In a study under a 70 year old Douglas fir forest, light fraction (LF) SOC decreased rapidly from 53% of total C (0-3 cm) to 33% of total C (3-13 cm) to 23% of total C (63-83 cm) (Spycher et al., 1983). In contrast, a study of two California soils of different mineralogy found that the LF (in this case, free + occluded LF, the latter obtained by sonication) decreased from 50-62% of total SOC content in the A horizon to 43-58% in the Bt horizon, but then increased to 63-67% of total SOC content in the BC horizon (Rasmussen et al., 2005). Lack of sonication in the methodology employed by Spycher et al. (1983) may explain the discrepancy between these studies. In fact, since roots have been observed to decompose more slowly with depth (Gill and Burke, 2002), it is not surprising to observe a greater proportion of LF SOC or POC with depth. In a deep soils study under Amazonian forest, fine root inputs (<1 mm) to the subsoil (1-8 m soil depth) were estimated at 90 g C m^{-2} with approximately 15% of deep soil C cycling on annual to decadal time scales (Nepstad et al., 1994).

Dissolved organic carbon and subsoil carbon saturation

DOC inputs to the subsoil are also hypothesized as an important contribution to C storage and cycling (Lorenz and Lal, 2005). Assuming an average annual flux of 200 kg DOC ha^{-1} yr^{-1} into the NT and FS soils from litter leachate (Table 3.5), then a 30 year flux would approximate 6 Mg C ha^{-1} from DOC. This is about 10% of the current 0-2 m soil profile content and demonstrates that DOC could play a substantial role in carbon content change at decadal time scales, at least in the surface horizon. This DOC flux from litter leachate is within the range of fluxes of 100-400 kg DOC ha^{-1} yr^{-1} reported for temperate forests (Michalzik et al., 2001). Of course, much of this DOC may be rapidly decomposed as opposed to being sorbed to mineral surfaces and protected from decomposition. On the other hand, greater connectivity among pores in NT or FS may lead to increased fluxes to nearly inaccessible micropores where DOC is then sorbed and protected from decomposition (Smucker et al., 2007). This theory is supported by data from NT but not FS, where the majority of the additional carbon content is found in the POC fraction. Again, it is possible that multiple mechanisms are at work in causing the difference in SOC profile contents.

Estimated DOC fluxes decreased by approximately an order of magnitude under all three land uses at 15 cm depth with an annual flux of 14, 13, and 28 kg DOC ha^{-1} under CT, NT, and FS, respectively. Annual DOC fluxes at 100 cm were estimated to be less than 1 kg ha^{-1}, which is partly due to a below average water flux during the monitoring period. Assuming DOC concentrations are representative of concentrations during the past three decades, then a 30 year net DOC input to the subsoil (15-100 cm) would amount to 1.2 and 0.5 Mg C ha^{-1} under FS and the agroecosystem, respectively (Table 3.6). This DOC input amounts to 4.4% of the current 15-100 cm SOC content under FS. A steady decline with depth in the amount of fine-C per unit of silt + clay suggests that the HSB soils are not saturated with SOC (Figure 3.4), according to the theory proposed by Hassink (1997). This is plausible, given that the HSB alluvial terrace probably formed sometime 11,000-30,000 yr BP, based on estimates of age from a chronosequence of alluvial deposits in northern Georgia, USA (Leigh, 1996). Thus, HSB is a relatively young soil and would take substantial time for deep soil to reach equilibrium with respect to DOC percolation and processing of POC inputs. Chronosequence work in Hawaii suggested that soils continued to accumulate carbon up to 150,000 yr with decline afterwards owing to loss of poorly-crystalline minerals of volcanic origin (Torn et al., 1997). These poorly-crystalline minerals have been shown to be tightly correlated with soil C contents for soils around the world (Kleber et al., 2005; Masiello et al., 2004; Rasmussen et al., 2005; Torn et al., 1997). The presence of poorly crystalline Fe and Al-oxides at HSB may play a similar role.

Conclusions

Results from HSB show that: (1) SOC has increased in no-till (NT) and forest succession (FS) relative to conventional tillage (CT) but that the majority of this change is concentrated in the upper 5 cm of the soil profile. The CT profile currently stores 20% less SOC than both the NT and FS profiles. The change in SOC contents is overshadowed by a massive accumulation of C in forest biomass that is three times the 0-2 m SOC content. In comparison, there was a noted lack of additional accumulation of SOC from crop residues returned annually to the soil in CT and NT compared to FS where biomass has accumulated aboveground. (2) The loss of SOC in

CT or storage in NT and FS could be linked to aggregate stability, which was enhanced under NT to 5 cm and under FS to 28 cm. (3) Land use impacted the DOC cycle with FS and NT litter leachate DOC fluxes more than double the CT DOC litter leachate flux at rates that could contribute 10% of the 0-2 m SOC content over 30 years. Although DOC fluxes were estimated to be higher under FS at 15 cm, they were an order of magnitude lower compared to the soil surface flux. Therefore, changes in subsoil C content due to a change in DOC flux at HSB would be difficult to detect after a century—even if all DOC was sorbed and protected by mineral association.

These results suggest that multiple mechanisms may be at work in the cycling and stabilization of SOC depending upon land use. The SOC content difference between the NT and CT profiles is largely contained in the fine (<53 μm) soil fraction while the majority of the difference between the FS and CT profiles is found in the POC fraction (53-2000 μm). In NT, lower C:N ratios from 0-5 cm, smaller subsoil SOC change, and a higher proportion of SOC in the fine fraction indicate that organic matter is more highly processed. As such, a substantial NT SOC pool may be stabilized as fine-C in aggregates by earthworm activity or by micro-scale fluxes of DOC that delivers carbon to micro-pores in NT but not CT where pore connectivity is disrupted by tillage. In FS, higher C:N ratios and POC concentrations through 2 m suggest that root inputs and/or bioturbation may be the primary drivers of deeper SOC change with water-stable aggregates protecting POC from decomposition near the surface. Downward translocation of POC through earthworm mediated translocation and greater subsoil root production, turnover, and recalcitrance may play a greater role in increasing subsoil SOC contents than percolation of DOC.

While differences in SOC content are concentrated near the surface, dynamic changes in C cycling extend well below the plow layer. Studies that focus only on differences in total SOC content easily overlook these intriguing, deep soil changes.

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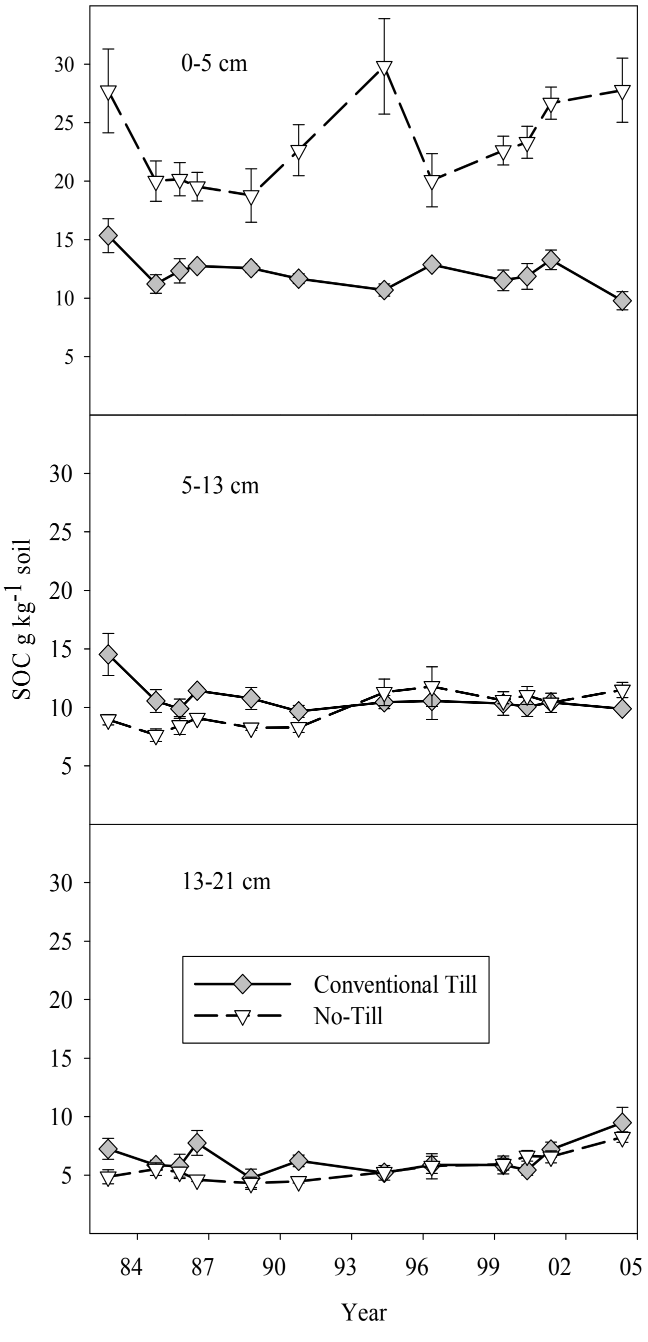

Figure 3.1. Soil organic C (SOC) measured in the Horseshoe Bend agroecosystem experiment (n=4) in Athens, GA, USA, 1982-2004. Data (means ± 1 SE) are not available from the beginning of the agroecosystem experiment in 1978.

Figure 3.2. Aerial photographs of the Horseshoe Bend agroecosystem plots, Athens, GA, USA, 1938-1999. Natural succession began in all experimental plots in 1966. The agroecosystem plots (blue and red) were cleared of natural successional vegetation in 1978 when the long-term experiment was begun. Natural succession continued in the forest succession (green) plots, although these plots were only established in 2007.

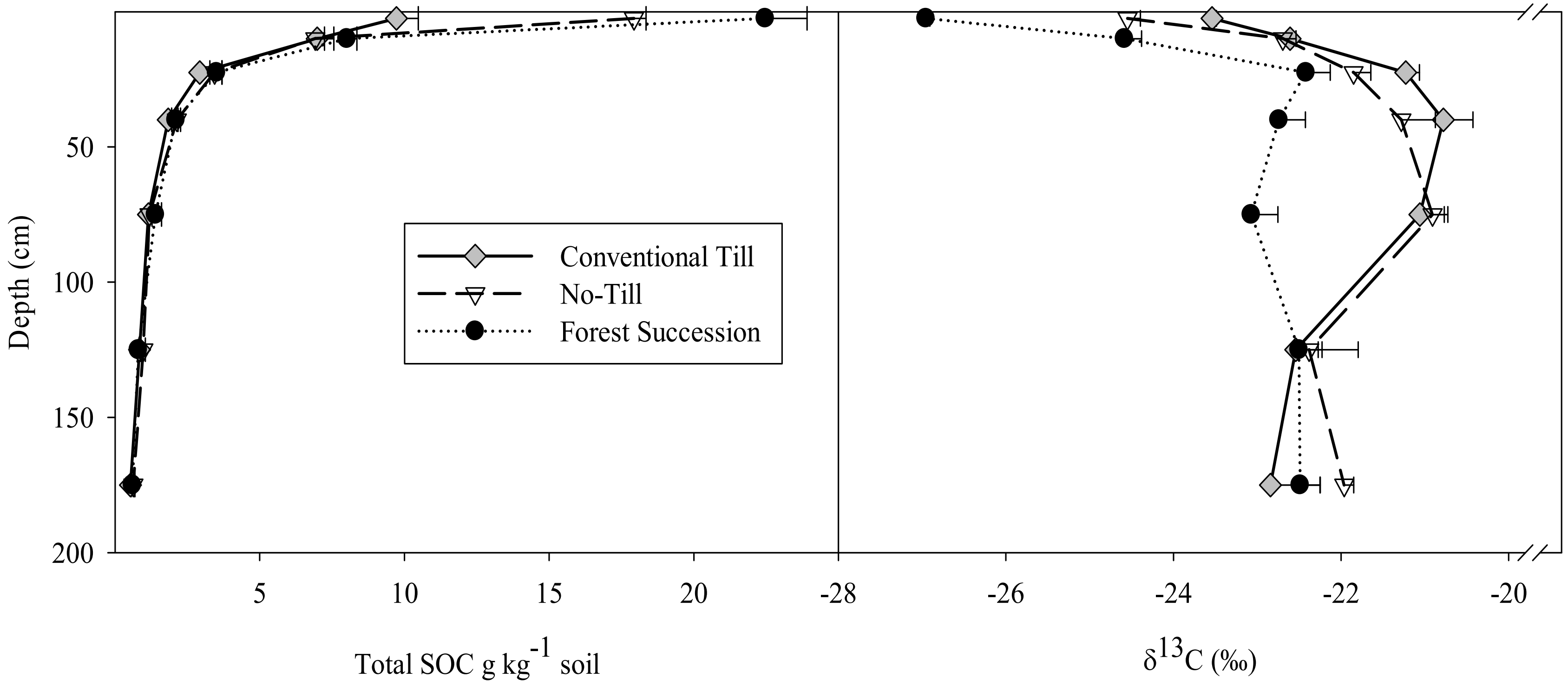

Figure 3.3. Total soil organic C (SOC) and its δ^{13} signature (means ± 1 SE) for the Horseshoe Bend agroecosystem experiment (n=4), Athens, GA, USA, March 2007

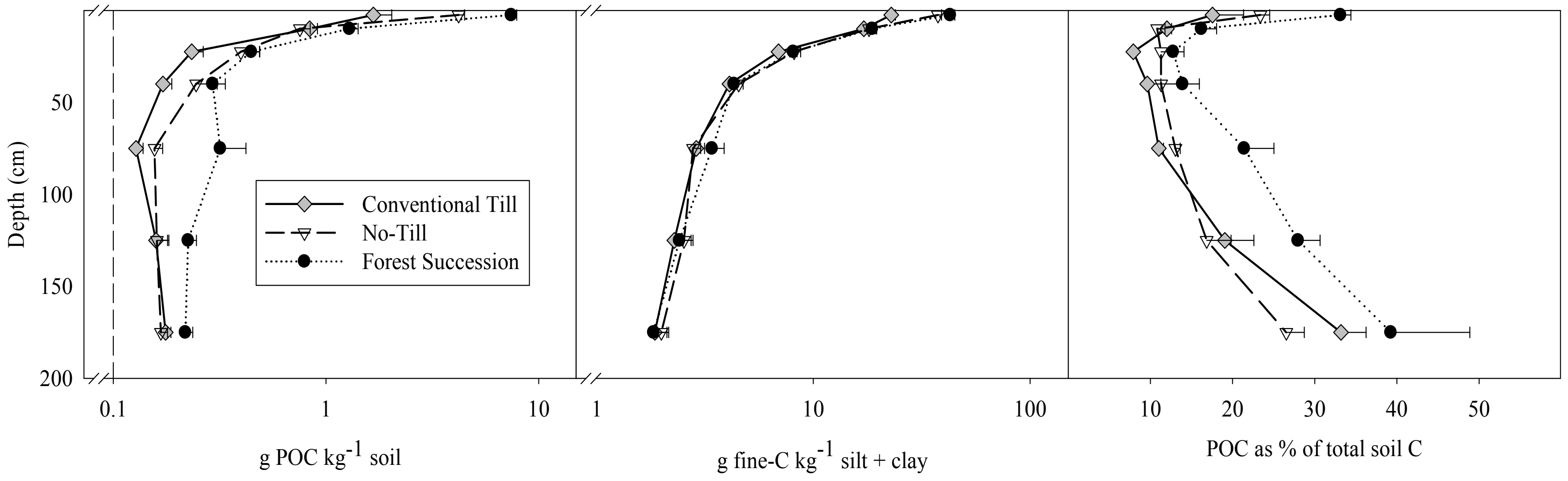

Figure 3.4. Particulate organic C (POC) and fine C (<53 µm) fractions (means ± 1 SE) at Horseshoe Bend, Athens, GA, USA, March 2007 (n=4). Fine-C is shown with respect to silt + clay to demonstrate extent of fine-C saturation with depth.

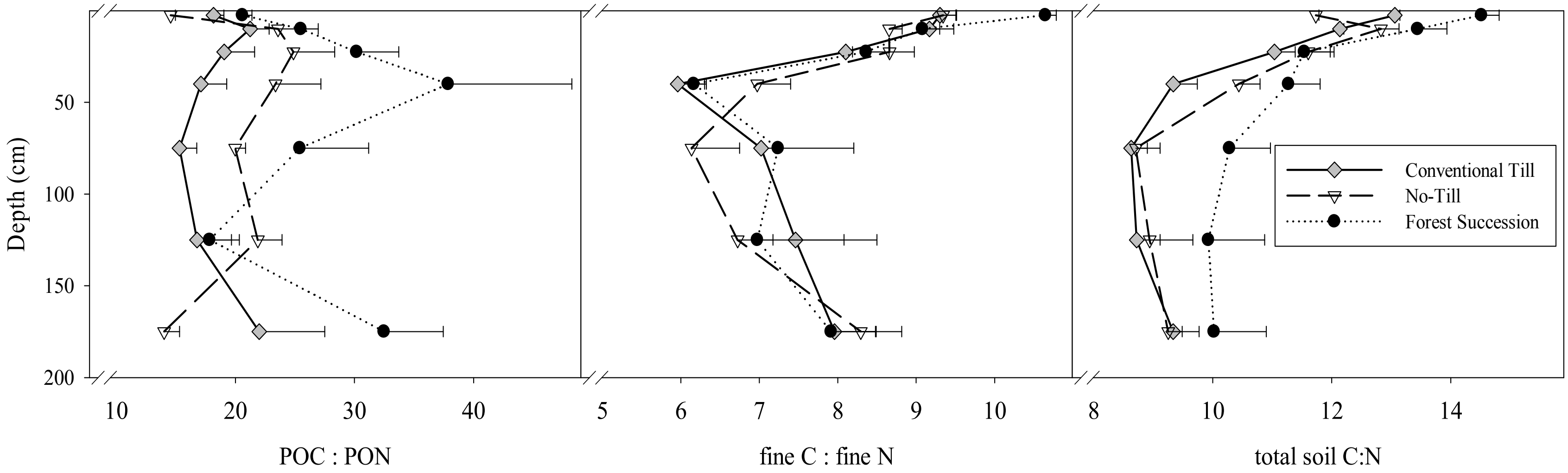

Figure 3.5. Particulate organic C: particulate organic N, fine-C:fine-N (< 53 µm), and total soil organic C:N (means ± 1 SE) for the Horseshoe Bend agroecosystem experiment (n=4), Athens, GA, USA, March 2007.

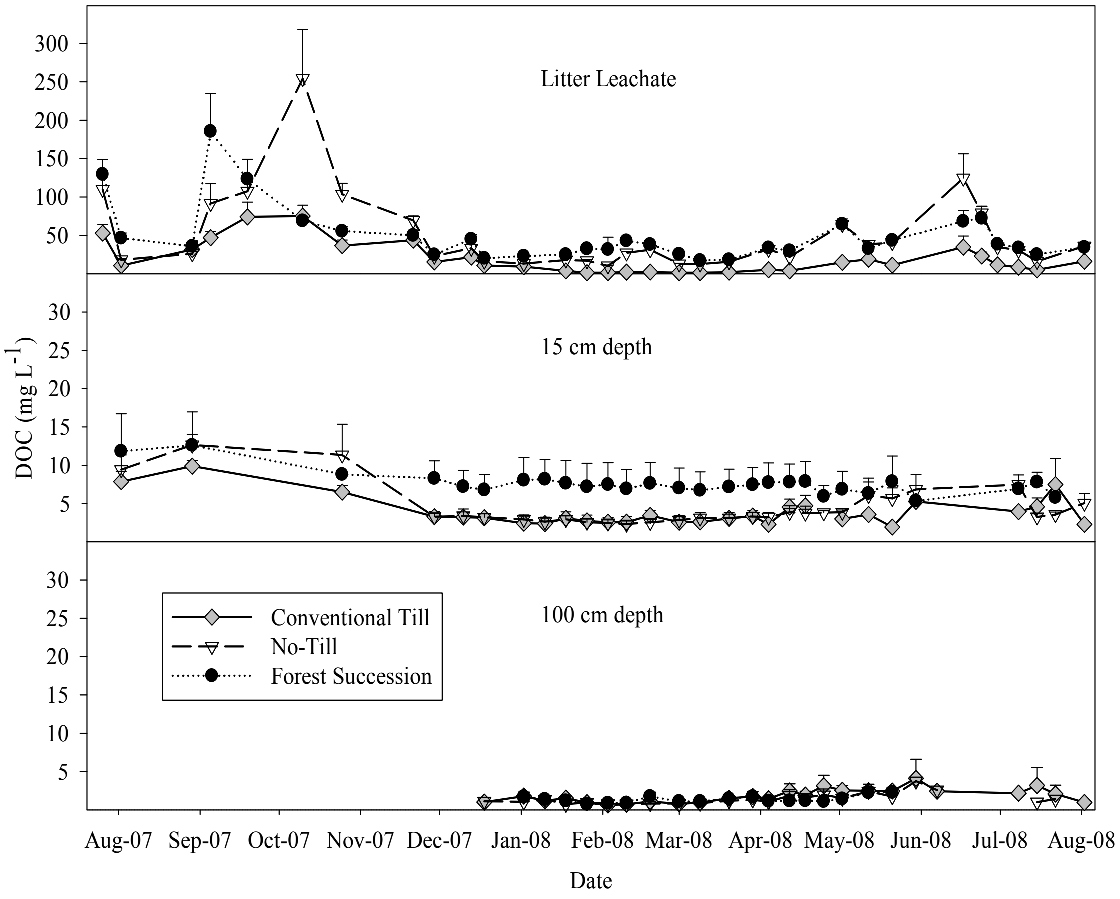

Figure 3.6. Dissolved organic C (DOC) concentrations (means ± 1 SE) for the Horseshoe Bend agroecosystem experiment (n=4), Athens, GA, USA.

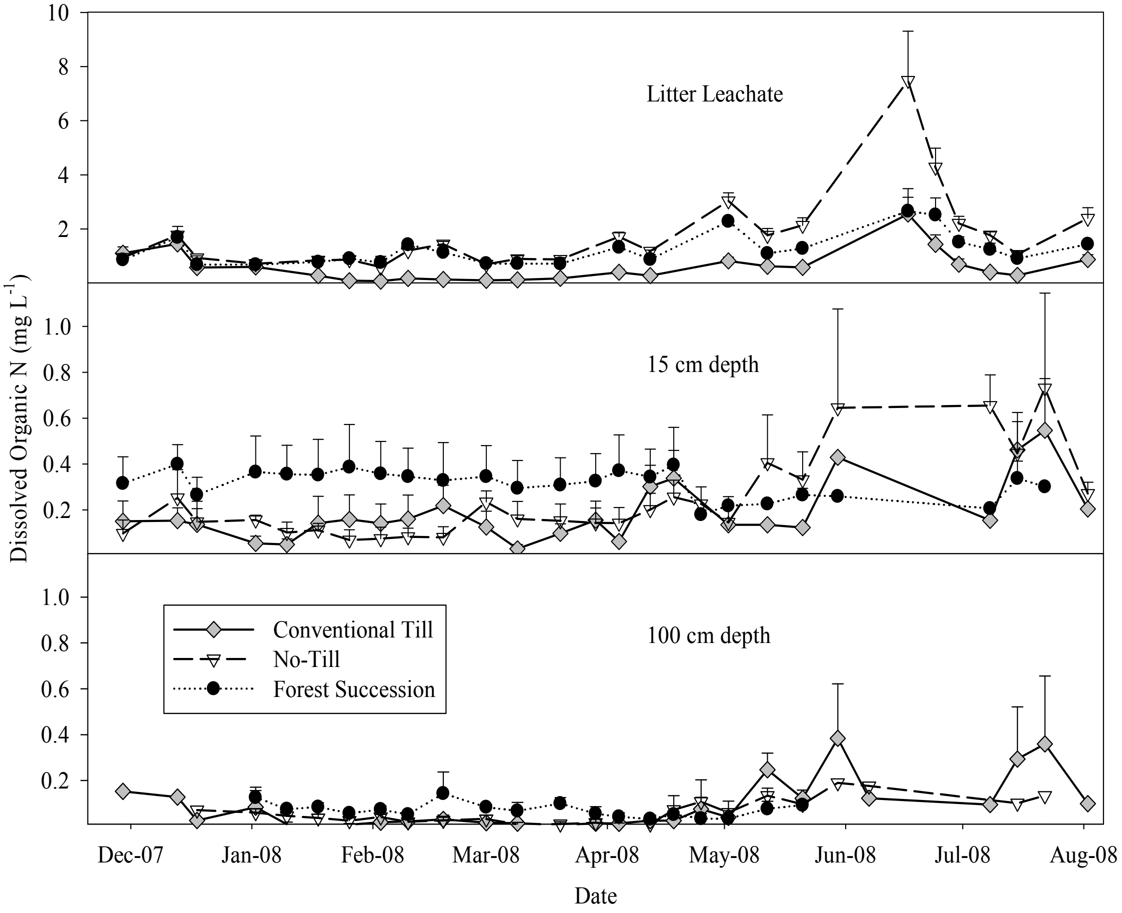

Figure 3.7. Dissolved organic N (means ± 1 SE) for the Horseshoe Bend agroecosystem experiment (n=4), Athens, GA, USA.

Table 3.1. Soil organic C (SOC) contents (means ± 1 SD) under three land uses in the Horseshoe Bend agroecosystem experiment (n=4), Athens, GA, USA, March 2007. Different letters within a depth and soil component indicate statistical significance between land uses based on Tukey's HSD with α=0.1. Particulate organic C (POC) + fine C (<53 μm) often exceed total C due to analytical error.

Land Use	*Depth*	*SOC*	*fine C*	*POC*	*total N*	*C:N*
	--cm--	---------------------------Mg ha^{-1}-----------------------				
CT	0-200	51.9 ± 4.9^{a}	45.7 ± 4.9^{a}	7.4 ± 0.7^{a}	5.1 ± 0.6^{a}	10.2 ± 0.3^{a}
NT		60.0 ± 4.5^{b}	51.0 ± 3.7^{a}	9.6 ± 1.1^{a}	5.8 ± 0.4^{a}	10.4 ± 0.2^{a}
FS		61.5 ± 4.3^{b}	49.1 ± 4.2^{a}	14.0 ± 1.6^{b}	5.3 ± 0.6^{a}	11.6 ± 0.5^{b}
CT	15-100	22.8 ± 1.6^{a}	21.1 ± 1.4^{a}	2.2 ± 0.2^{a}	2.4 ± 0.4^{a}	9.5 ± 0.7^{a}
NT		24.6 ± 1.1^{a}	22.4 ± 1.2^{a}	3.0 ± 0.7^{ab}	2.5 ± 0.2^{a}	10.0 ± 0.4^{a}
FS		26.9 ± 1.8^{a}	23.3 ± 1.6^{a}	4.6 ± 2.1^{b}	2.5 ± 0.3^{a}	10.9 ± 0.6^{b}

Table 3.2. P-values for land use contrasts (Tukey's honestly significant difference) of total soil organic C (SOC), particulate organic C (POC), and fine C concentration differences by depth class. The 0-200, 15-100, and 15-200 cm depths are contrasts for SOC content. Horseshoe Bend agroecosystem experiment (n=4), Athens, GA, USA, March 2007.

Depth	SOC	POC	fine C	SOC	POC	fine C	SOC	POC	fine C
--cm--	---------*NT vs. CT*--------			----------*FS vs. NT*-------			-------------*FS vs. CT*-----------		
0-5	0.0005	0.003	0.001	0.02	0.0005	0.21	<0.0001	<0.0001	0.0002
5-15	0.99	0.83	0.99	0.22	0.01	0.59	0.25	0.03	0.66
15-30	0.40	0.19	0.47	0.98	0.85	0.99	0.32	0.08	0.40
30-50	0.19	0.50	0.28	0.98	0.74	0.50	0.25	0.19	0.88
50-100	0.98	0.94	0.97	0.54	0.19	0.87	0.43	0.11	0.76
100-150	0.32	0.99	0.43	0.16	0.14	0.11	0.87	0.13	0.62
150-200	0.42	0.89	0.49	0.91	0.07	0.64	0.64	0.14	0.96
0-200	0.08	0.07	0.24	0.89	0.001	0.81	0.04	<0.0001	0.52
15-100	0.69	0.68	0.79	0.54	0.22	0.91	0.18	0.06	0.54
15-200	0.40	0.67	0.48	0.96	0.03	0.86	0.29	0.008	0.79

Table 3.3. P-values (Tukey's honestly significant difference) for land use contrasts of δ^{13}C signatures and C:N ratios by depth class in the Horseshoe Bend Agroecosystem experiment (n=4), Athens, GA, USA, March 2007.

Depth	δ^{13}C (‰)	soil C:N	fine-C:N*	POC:N†	δ^{13}C (‰)	soil C:N	fine-C:N	POC:N	δ^{13}C (‰)	soil C:N	fine-C:N	POC:N
--cm--	---------------------*NT vs. CT*--------------------				---------------------*FS vs. NT*------------------				---------------------*FS vs. CT*------------------			
0-5	<0.0001	0.001	0.99	0.01	<0.0001	<0.0001	0.001	0.0005	<0.0001	0.0007	0.001	0.09
5-15	0.92	0.36	0.38	0.58	<0.0001	0.43	0.50	0.69	<0.0001	0.05	0.97	0.20
15-30	0.18	0.60	0.31	0.44	0.23	0.99	0.69	0.50	0.01	0.67	0.75	0.09
30-50	0.60	0.23	0.13	0.78	0.04	0.40	0.25	0.30	0.01	0.03	0.90	0.11
50-100	0.93	0.99	0.63	0.62	0.004	0.12	0.50	0.53	0.005	0.10	0.97	0.15
100-150	0.96	0.98	0.84	0.38	0.98	0.62	0.98	0.53	0.997	0.49	0.93	0.96
150-200	0.27	0.99	0.90	0.43	0.60	0.63	0.88	0.04	0.79	0.69	0.99	0.25

*particulate organic C (POC) : particulate organic N (PON)

†fine-C : fine-N (<53 μm)

Table 3.4. Mean-weight diameter (MWD) for dry and wet aggregates (means ± 1 SD) at Horseshoe Bend Agroecosystem Experiment (n=4), Athens, GA, USA, October 2007. Different letters indicate statistical significance between land uses within a depth class based on Tukey's HSD with α=0.1.

Depth cm	*Land use*	*Dry MWD*	*Wet MWD*	*Stability index* Wet/Dry
		----------mm	----------	
0-5	Conventional Till	3.1 ± 0.3^a	2.2 ± 0.4^b	0.73 ± 0.10^b
	No-Till	3.6 ± 0.4^a	3.5 ± 0.4^a	0.96 ± 0.04^a
	Forest Succession	3.6 ± 0.9^a	3.6 ± 0.9^a	0.98 ± 0.01^a
5-15	Conventional Till	4.2 ± 0.3^a	3.2 ± 0.4^a	0.77 ± 0.08^b
	No-Till	4.5 ± 0.2^a	3.7 ± 0.2^a	0.82 ± 0.06^b
	Forest Succession	4.2 ± 0.7^a	3.9 ± 0.7^a	0.94 ± 0.01^a
15-28	Conventional Till	4.5 ± 0.3^a	1.7 ± 0.1^b	0.37 ± 0.06^b
	No-Till	4.4 ± 0.4^a	1.9 ± 0.3^b	0.42 ± 0.03^b
	Forest Succession	4.5 ± 0.6^a	2.7 ± 0.5^a	0.60 ± 0.04^a

Table 3.5. Fluxes (means ± 1 SD) of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in litter leachate (0 cm), and 15 and 100 cm soil solutions in the Horseshoe Bend agroecosystem experiment (n=4), Athens, GA, USA, Aug-2007-Aug-2008. Precipitation during the monitoring period was 89.4 cm. Different letters within a depth and solution component indicate statistical significance between land uses based on Tukey's HSD with $\alpha=0.1$.

Land Use	Depth	H_2O	DOC[*]	DON[†]	DOC:DON[††]	DON
	------cm------		--------kg ha^{-1} yr^{-1}--------			--% of TDN--
CT	0	67.1	81 ± 23^{a}	3.3 ± 1.0^{a}	17 ± 1^{a}	44 ± 6
NT			196 ± 22^{b}	8.6 ± 1.3^{c}	19 ± 1^{a}	49 ± 8
FS			211 ± 42^{b}	6.4 ± 1.2^{b}	29 ± 2^{b}	57 ± 8
CT	15	34.3	14.0 ± 4.7^{a}	0.69 ± 0.55^{a}	25 ±15^{a}	9 ± 9
NT			12.9 ± 3.4^{a}	0.76 ± 0.18^{a}	15 ± 1^{a}	19 ± 19
FS			28.4 ± 16.1^{a}	1.31 ± 0.87^{a}	23 ± 7^{a}	75 ± 37
CT	100	6.6	0.94 ± 0.37^{a}	0.02 ± 0.01^{a}	26 ± 7^{a}	6 ± 8
NT			0.82 ± 0.38^{a}	0.03 ± 0.01^{ab}	30 ± 9^{b}	14 ± 21
FS			0.91 ± 0.40^{a}	0.05 ± 0.02^{b}	17 ± 5^{ab}	58 ± 33

[*] Annual flux based on volume-weighted concentrations from annual collection

[†] DON = total dissolved nitrogen (TDN) – (NO_3-N + NH_4-N). Annual flux estimate based on volume-weighted concentrations from 9 month collection (Nov-07 to Aug-08)

[††] Calculated from Nov-07 to Aug-08 collections.

Table 3.6. Annual net input of dissolved organic carbon (DOC) to the subsoil (15-100 cm) averaged for CT and NT treatments (Agroecosystem) and for Forest Succession using concentration data from Aug. 2007 to 2008 and the average annual water flux from model simulation with HYDRUS (1978-2007). Horseshoe Bend Agroecosystem Experiment, Athens, GA, USA (n=4 per treatment).

Land use	*DOC*		*15-100 cm*
	15 cm	100 cm	DOC net input†
	----------------------kg ha^{-1} yr^{-1}----------------------		
Agroecosystem	19.5	2.0	17.5
Forest Succession	41.2	2.1	39.1

†DOC net input = 15 cm flux – 100 cm flux

CHAPTER IV

SOIL ACIDIFICATION THROUGH TWO METERS DURING FOREST SUCCESSION ALONGSIDE A 30-YR AGROECOSYSTEM EXPERIMENT [2]

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[2] Scott Devine, Daniel Markewitz, Paul Hendrix, and David Radcliffe. To be submitted to: *Ecological Applications*

Abstract

A mass-balance approach was used at the Horseshoe Bend (HSB) agroecosystem experiment in the piedmont of Georgia, USA, to compare mechanisms of soil acidification under forest succession (FS), no-tillage (NT) and conventional tillage (CT) management. It was hypothesized that FS would lead to greater rates of soil acidification due to forest nutrient demands and higher rates of base cation leaching driven by greater production of organic acids and HCO_3 at depth. Exchangeable cations and pH were measured from 0 to 200 cm and fertilizer application and forest uptake of base cations were estimated. Solutions were analyzed at 0, 15, and 100 cm for major cations and anions. Results show a significant contrast between the FS and the agroecosystem soil profiles—not between CT and NT—with significantly lower 0-2 m exchangeable contents of Ca, Mg, and K under FS. In contrast, the FS soil is more acidic through 2 m. When removal of Mg and K by forest uptake from the FS soil exchangeable pool is considered, then elevated Mg and K in the agroecosystem soil profile is less than applications of these nutrients in fertilizer to the agroecosystem. This suggests enhanced leaching of Mg and K under the agroecosystem. Solution data do show greater leaching of base cations under the agroecosystem linked to greater production of NO_3 and HCO_3 with organic acids contributing only a minor amount to anionic charge in deeper soil solution under all land uses. However, specific leaching rates needed to explain the missing fertilizer Mg and K are not supported by past or current estimates of leaching rates from the agroecosystem. Complicating the results, the lower soil exchangeable Ca content under FS is not fully explained by uptake in forest biomass and lack of fertilizer input. This suggests that forest uptake of Ca may currently be underestimated. Multiple processes have shaped the soil profile chemistries at HSB, including forest uptake, applications of fertilizer to the agroecosystem, and leaching.

Introduction

Since the onset of the industrial revolution, combustion of fossil fuels has increased atmospheric concentration of sulfuric and nitric acids (Galloway, 2001). At the same time, modern cropping regimes that use ammonium based fertilizers and legumes to boost soil N have increased rates of nitrification and nitrate salt leaching (Moody and Aitken, 1997; Ridley et al., 1990). These anthropogenic factors of soil acidification have led to concern over effects on water quality (Burns et al., 1981), forest productivity (Likens et al., 1996), and soil productivity in pastures and croplands around the world (Juo et al., 1995; Noble et al., 2002).

Soil acidification, defined as either a decrease in soil pH or a reduction in base saturation of the exchange complex, is a natural process necessary for crustal weathering to occur and for the production of soil bodies from rock. There are five major natural soil acidification processes: soil respiration and the concomitant generation of carbonic acid; the production of organic acids from microbial and root biochemistries; nitrification of ammonium to produce nitric acid; oxidation of sulfides in primary minerals and of organic sulfur in soil organic matter to produce sulfuric acid; and a preferential uptake of base cations over anions by plants (Binkley and Richter, 1987; Richter and Markewitz, 2001). How land use affects these processes is important to understanding the effects of management on long-term soil productivity.

Increases in soil acidity as a result of afforestation have been documented for reforestation of agricultural land around the world, including the southern US piedmont (Richter and Markewitz, 2001), southeastern US coastal plain (Markewitz et al., 2002), the northeastern United States (Driscoll and Likens, 1982), Europe (Alriksson and Olsson, 1995; Ritter et al., 2003), and the tropics (Farley et al., 2008. Work on the mechanisms of soil acidification in areas of afforestation has suggested that internal ecosystem function is as important as acidic deposition in affecting soil change. A comparison of whole-tree harvesting versus leaching showed that for the majority of the sites plant uptake and removal would have a greater effect on limiting nutrient cations than leaching (Johnson et al., 1988). A proton budget approach suggested that after 34 years of *Pinus taeda* growth on an Ultisol, 44% of the acidification was due to base cation uptake by vegetation, 15% due to production of carbonic acid from soil respiration, and the remaining 41% was attributed to acidic deposition and associated leaching (Markewitz et al., 1998). Export of cations through tree biomass in South American plantations demonstrated substantially reduced exchangeable cation pools compared to adjacent grassland soils, resulting in stream acidification as percolating water now makes contact with a soil matrix of lower base saturation (Farley et al., 2008). Although leaching of base cations under the grassland was greater due to higher base saturation, the flux of base cations through tree biomass removal was of a much greater magnitude than stream exports draining grasslands (Farley et al., 2008).

In contrast to these reports of soil acidification following afforestation, no reduction of exchangeable soil Ca^{2+} was evident fifteen years after a whole-tree harvest followed by forest re-growth, even though vegetation uptake by itself could have reduced exchangeable Ca^{2+} by 40% (Johnson and Todd, 1998). The authors speculated that either the exchangeable pool had been replenished via the non-exchangeable pool or that roots in the aggrading forest had accessed deeper soil pools of Ca^{2+} to meet its nutrient demands (soils were sampled to 45 cm). Similarly, high rates of nitrification and associated base cation leaching appeared to be buffered by non-exchangeable mineral pools in the western United States under Red Alder (Homann et al., 1992). Recent work in the northeastern United States has illustrated that mechanisms of soil acidification are still poorly understood (Bailey et al., 2005). In this work, the researchers identified large pools of “lost” exchangeable Ca^{2+} at two of four studied forested sites that had been sampled thirty years earlier. The authors concluded that forest uptake could not account for soil change at the sites with the highest loss, implying that leaching was responsible. In criticism that followed this work, it was estimated that leaching rates of Ca^{2+} at these sites would have had to have been 6.1 to 19 $kmol_c$ ha^{-1} yr^{-1} to account for the change, much greater than estimated annual deposition of SO_4^{2-} and N in that part of the world and greater than previously estimated leaching rates for this region (0.5-2 $kmol_c$ ha^{-1} yr^{-1}) (Johnson, 2005). However, rates of Ca^{2+} leaching have been estimated to be as high as 24 $kmol_c$ ha^{-1} yr^{-1} at forests in Washington, USA, due to high soil base saturation and high concentrations of HCO_3^- (Johnson et al., 1988), demonstrating the importance of inherent soil properties in determining rates of soil acidification.

In order to predict the long-term effects of “acid rain” and land management, much effort has gone to developing models that predict the effects of acidification mechanisms on soil and water chemistry (Cosby et al., 2001; Reuss and Johnson, 1986; Verburg and Johnson, 2001). The basis of these models is the law of charge balance, which states that total cation charge must always equal total anion charge for a solution in equilibrium, and how it interacts with the soil exchange complex. Employing this conceptual model, the export of cations is expected to increase whenever the concentration of anions in solution is increased. The rate of base cation leaching (Ca^{2+}, Mg^{2+}, K^+, and Na^+) will also be greatest in soils with high base saturation of the exchange complex. In this work, generation of HCO_3^- from dissolved CO_2, production of NO_3^- from nitrification, and production of organic acids by microbes and plants are given special attention, since they are expected to be the most land-use dependent of the dominant anions in soil waters.

The overall objective of this work is to estimate the extent to which soil acidification mechanisms have contributed to changes in soil exchange chemistries at Horseshoe Bend (HSB), Athens, GA, USA. HSB is a 30-yr-old agroecosystem experiment that has compared soil attributes under conventional and no-till agriculture, including early soil solution monitoring and measurement of soil exchange chemistry (Stinner et al., 1984). In the current study, land adjacent to the agroecosystem experiment that has undergone forest succession is again added to the comparison, as done previously (Stinner et al., 1984). To address mechanisms of acidification, soils were sampled to 2 meters and exchangeable cation concentrations and pH were measured. Fertilizer applications to the agroecosystem plots were also estimated. Assuming atmospheric deposition was the same to the agroecosystem and aggrading forest at HSB, it was hypothesized that greater production of HCO_3^- and organic acids at depth associated with deeper forest roots, as well as continuous base cation uptake by a rapidly growing forest, would lead to greater soil acidification during forest succession than under continuous agriculture. Also, following results from an earlier study at HSB where leaching of some nutrients (Ca and N) were greater under conventional tillage compared to no-till agriculture, it was again hypothesized that no-till systems may more efficiently cycle nutrients than conventional tillage systems (Stinner et al., 1984). If so, this process should have resulted in significantly lower exchangeable cation contents in the conventional tillage soil profile.

Methods

Site Description

The Horseshoe Bend (HSB) agroecosystem experiment (33° 57' N, 83° 23'W) in Athens, GA, USA, is a long-term comparison of conventional and no-tillage treatments begun in 1978.

Based on a series of aerial photos, HSB had been cleared entirely of trees except for a narrow strip along the Oconee River at least since 1938 (Figure 3.2). The site was probably used by Native Americans for agriculture in its earliest history, since they preferred bottomlands for cultivation but more recently was used for pasture and forage production until 1965 when the Institute of Ecology acquired HSB for research (Hendrix, 1997). The area underwent secondary succession in 1966 except for the future agroecosystem site, which was tilled to plant a crop of millet for a separate, earlier study (Barrett, 1968). Afterwards, the future agroecosystem site went fallow and was used for a prescribed burn study and a N fertilization study (Bakelaar and Odum, 1978; Odum et al., 1973). In 1978, the study area was divided into equal numbers of conventional and no-till 0.1 ha plots, and the old-field vegetation was mowed (Hendrix, 1997). Since the experimental plots were in fallow from 1966, the current no-till plots have not been tilled for forty-two years.

Conventional tillage has been performed twice annually in most years with moldboard plowing to a depth of 15 cm, followed by disking. In 1978 and 1979, fertilizer was applied with limestone as a carrier (Stinner et al., 1984), which was reported as an application of 75 kg Ca ha^{-1} yr^{-1} (Stinner, 1981). In 1980, 2300 kg ha^{-1} of dolomitic limestone ($MgCa(CO_3)_2$) was applied (Groffman et al., 1987), which is the only recorded liming event during the agroecosystem experiment. NPK fertilizer has also been applied intermittently but more heavily in the 1980s (Hendrix, 1997). In 1981, each agricultural plot was split into different winter crop treatments with winter rye (*Secale cereale* L.) grown on half of each plot and N-fixing crimson clover (*Trifolium incarnatum* L.) grown on the other half until 1984 and then again from 1989 to the present (Coleman et al., in press; Hendrix, 1997). In my soil sampling efforts, I sought to estimate an average effect of no-tillage and conventional tillage on the measured properties by sampling equally between clover and rye split-plots before compositing.

Three secondary, hardwood forest plots adjacent to the tillage experiment and a fourth afforested plot approximately 80 m to the west of the experiment were established in 2007 (Figure 3.2). These areas were intended to represent a third treatment, referred to henceforth as forest succession. All plots were on the same terrace as the agroecosystem plots and observed to be part of the same cleared area in the aerial photograph (Figure 3.2). Most likely, these afforested plots were not tilled in 1966, which means they essentially underwent a pasture to forest conversion. The soils under all three land uses have been re-classified from a clayey, kaolinitic, thermic, Rhodic Kanhapludult (Beare et al., 1997) to a fine-loamy, kaolinitic, thermic, Typic Kanhapludalf based on new particle-size analysis data in the control section and measurements of base saturation that were >98% in all three treatments at 140 cm (i.e., 125 cm below the top of the kandic horizon).

Soil sampling and analysis

In March 2007, soil profiles were sampled in each of the twelve experimental plots (n=4 per treatment) in seven depth classes: 0-5, 5-15, 15-30, 30-50, 50-100, 100-150, and 150-200 cm. To sample the 0-50 cm depth classes, a 2.2 cm diameter slide hammer coring device was used to obtain five cores from each plot: two cores from each split-plot of rye and clover and one core on the border between the split-plots. In the agricultural plots, one hole was augered in the center of each plot on the split-plot border between the clover and rye crops to sample the 50-100, 100-150, and 150-200 cm depth classes. Two holes were augered in each forested plot and were composited by depth class. These samples were air-dried, crushed with a rolling pin, and then passed through a 2 mm sieve to remove coarse material. Separate bulk density samples were collected in September 2008. Two 7.5 cm diameter by 5 cm depth cores per plot were collected for the 0-5 cm depth class (n=24). Two additional 7.5 cm diameter by 7.5 cm height cores were collected within the 5-15 cm (i.e., 6-13.5 cm) depth (n=24). In the 15-30 cm layer one core per plot from 19-26.5 cm (n=12) was obtained. For 30-50 and 50-100 cm in half of the plots for each land use, one core was collected from 36-43.5 cm and another from 71-78.5 cm (n=6 per depth class).

Earlier mineralogical work on subsamples showed no evidence of carbonates so no pre-treatments were performed (Devine, unpublished data). Soil pH_{H20} was measured in a 20 g: 20 ml (soil:H_2O) slurry followed by addition of 0.20 ml 1 M $CaCl_2$ to adjust to a 0.01 M $CaCl_2$ solution for measurement of pH_{CaCl2} (Thomas, 1996). Exchangeable acidity was extracted by shaking 5.0 g soil in 50 ml 1 M KCl for 30 minutes and then filtering the extract with a Whatman 42 filter paper (Thomas, 1982). The extracts along with five filtered KCl blanks were titrated with an auto-titrator to pH 8.2 with 0.02 M NaOH to quantify the amount of exchangeable acidity. Exchangeable Ca, Mg, and K were extracted with dilute double acid solution (0.05 N HCl + 0.025 N H_2SO_4) (Mehlich, 1953) and measured by atomic adsorption.

Solution sampling and analysis

Wet-fall, litter leachate and soil solutions were collected every 7-10 days. One automated, battery-powered dry fall-wet fall collector (Aerochemetrics Bushnell, FL) was placed in the middle of the agroecosystem experiment to collect wet-fall precipitation. Three bulk precipitation collectors were also placed in open areas but persistent bird-dropping contamination invalidated chemical concentrations, although volumes were utilized. Litter leachate was collected with PVC pipes and matching end-caps that were cut into thirds and fashioned into 9 cm x 30 cm troughs connected by polypropylene tubing to a 4 L bottle stored in a hole. Pieces of aluminum flashing were used as covers for the holes to protect litter leachate solution from direct sunlight. The thin O-horizons (<0.5 cm) under each PVC trough in forest succession and no-till plots were cut before installation and placed into the collector. For the CT and NT plots, one collector was installed in a rye split-plot and the other in a clover split-plot. Each litter leachate sample was analyzed separately with plot sub-samples averaged together before statistical analysis. To collect soil solution, two Prenart Super Quartz tension lysimeters (Prenart Equipment Aps, Frederiksberg, Denmark) connected to 2 L Nalgene bottles were installed in each plot: one at 15 cm depth and the other at 100 cm depth. Lysimeters were divided evenly between clover and rye split-plots for the conventional till and no-till treatments. A 90° PVC triangle was used to guide an auger into the ground at a 45° angle to avoid disturbing the soil profile directly above the lysimeter. A punch tube with the same diameter as the lysimeters was used to make the final hole where the lysimeters were installed at the bottom of the augered hole. A slurry of acid-washed silica flour was also used around each lysimeter to ensure good contact with the soil matrix. The holes were back-filled with soil carefully returned in the same order as it was removed. Twice each week when soil moisture was sufficient for collection, tensions of -0.065 to -0.0750 MPa were established in each lysimeter-bottle combination with a hand vacuum pump.

All samples were collected on the same day, with a portion filtered through Whatman 0.45 μm polycarbonate filters, and refrigerated until analysis. Remaining unfiltered samples were analyzed for conductivity, $pH_{initial}$, $pH_{degassed}$, and titratable alkalinity. A method used for stream water samples was modified to measure alkalinity via a gran-titration plot (Neal, 1988). Briefly, sample volumes were gravimetrically determined and then auto-titrated with a 0.001 M HCl titrant to an end-point of 4.0. Gran alkalinity was calculated by linear regression of cumulative acid added to the sample in μeq H^+ (x-axis) to measured H^+ (y-axis) for the last 5 pH readings (pH 4.5 to 3.9) of the titration. Measured H^+ in μeq is calculated by multiplying the total sample volume (initial volume + volume of added acid) by the H^+ μeq L^{-1} estimated from the pH reading. The x-intercept of this regression is equal to the alkalinity in total be HCO_3^- neutralized by the added acid. Dividing this by the initial sample volume allowed for expression of alkalinity in μeq L^{-1}.

Analyses of filter samples included total nitrogen and non-purgable organic carbon by acidification to pH 2 and sparging with CO_2-free air for 3 minutes (Shimadzu TOC 5000, Columbia, Maryland, USA). Analysis for NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, $SO4^{2-}$, PO_4^{3-} and $NO3^-$ was on a Dionex DX 500 Ion Chromatograph (Dionex, Sunnyvale, CA). TN and NPOC were analyzed from Aug 2007 to 2008 while ion chromatographic analysis only extended from Nov 2007 to Aug 2008. By convention, the contribution of charge from organic anions was first estimated to be equal to the anion charge deficit, defined as the sum of charge from major cations minus the sum of charge from major anions (Cronan et al., 1978):

$$\text{Anion deficit} = 2(Ca^{2+}) + 2(Mg^{2+}) + (Na^+) + (K^+) + (NH_4^+) + (H^+) - 2(SO_4^{2-})$$
$$- (Cl^-) - (NO_3^-) - (HCO_3^-) - 3(PO_4^{3-})$$

Estimation of HCO_3^- by alkalinity titrations is known to be confounded by presence of organic acids with pK_a values that overlap the pK_a of the bicarbonate end point (about 4.5) (Drever, 1997). In litter leachate samples with high dissolved organic carbon concentrations, the anionic charge measured as alkalinity may be primarily due to partial protonation of organic species during the titration. Thus, a second estimation of the contribution of charge from organic anions was made that ignored the alkalinity titration and contribution of HCO_3^- to anionic charge, defined in this work as the strong acid anion deficit:

$$\text{Strong acid anion deficit} = 2(Ca^{2+}) + 2(Mg^{2+}) + (Na^+) + (K^+) + (NH_4^+) + (H^+) - 2(SO_4^{2-}) - (Cl^-) - (NO_3^-) - 3(PO_4^{3-})$$

Charge balance

The theoretical basis of the acidification models is the law of charge balance. It states that total negative charge must equal total positive charge for a solution to be in equilibrium (Drever, 1997). Thus, by tracking atmospheric inputs of NO_3^-, Cl^-, and SO_4^{2-}, generation of additional NO_3^- from nitrification, HCO_3^- from soil respiration, and enrichment of solution with organic acids from throughfall, litter leachate, and microbial activity, total cation charge in soil solution can be predicted. The cations that come into solution are either basic (Ca, Mg, K, Na, and NH_4) or acidic (H, Al^{3+}, $Al(OH)_2^{2+}$, etc.), which is determined principally by percent base saturation of the exchange complex, and can be predicted mathematically by the Gapon or Gaines-Thomas expressions, along with selectivity coefficients that describe the charged soil surfaces' affinity for each cation species (Cosby et al., 2001).

Hydrologic Fluxes

The goal of estimating hydrologic fluxes was not to separate treatment effects on water flow through the soil but to scale concentration data from lysimeters to a field-scale flux. Fluxes were modeled from 1978 to 2008. Details of the model are in Devine (2009: Appendix A). In brief, to estimate hydrologic flux a one-dimensional model created in HYDRUS (2D/3D) version 1.02 (Simunek et al., 2007) was utilized. The 1 m model profile was divided into five layers to match the soil depth classes described previously, which were discretized into 1 cm vertical increments. Soil hydraulic parameters (θ_r, θ_s, α, n, and K_s) for each layer were estimated based on textural class and bulk density data using the Rosetta Lite v.1.1 tool that accompanies HYDRUS (2D/3D) (van Genuchten, 1980). Potential evapotranspiration (PET) based on the Penman-Monteith method was estimated using ETo Calculator (Raes and Munoz, 2008). A second estimate of PET was made using the Thornthwaite method (Thornthwaite, 1948). All climactic data were either from the Athens Ben Epps Airport (33°57' N, 83°20' W) available through the National Climactic Data Center (NCDC, 2007) or from preliminary data available through the National Weather Service (NWS, 2008). Modeled actual evapotranspiration was based on the Feddes water uptake reduction model with parameters based on *Zea mays* and taken from a database that accompanies HYDRUS (2D/3D). Generation of an internal mesh-line available in HYDRUS (2D/3D) at 15 cm depth allowed for estimation of a water flux at 15 cm (Simunek et al., 2007). HYDRUS (2D/3D) automatically generates an output file for the free drainage boundary in the model, which allowed for estimation of the water flux at 100 cm depth. Since no on-site data were available to either calibrate or verify the model, modeled soil tensions at both 15 and 100 cm were graphed to assure periods of low and high tension matched periods of lysimeter collections in the field.

Aboveground forest biomass: cation contents

Tree cation contents were estimated by allometric equations based solely on DBH for *Carya spp., Liquidambar styraciflua* L., and *Quercus nigra* L. (Phillips et al., 1989). On average, these three species accounted for 85% of the total biomass by plot (Devine 2009). These estimates were then adjusted for remaining biomass in each plot, so that total Ca, Mg, and

$K = N_p*(B_t/B_p)$ where N_p is the nutrient content of the subset of the biomass included in the initial estimate, B_t is the total plot biomass estimate, and B_p is the subset of the biomass represented by the three tree species listed above.

Statistical Analysis

Overall differences in 0-2 m sums of exchangeable Ca, Mg, K, and exchangeable acidity were tested with a one-way ANOVA with land use as the main effect (n=4). Two response variables (pH_{H2O} and pH_{CaCl2}) which could not be summed quantitatively for the whole profile were analyzed first as a split-plot design with land use (CT, NT, and FS) as the main effect and depth as the split factor. Since we also expected that land use effects might be limited to the shallow soil layers and that variability in subsoil cation contents might overshadow these surficial divergences, treatment effects were also evaluated by performing the same ANOVA for each of the seven depth classes (n=4). For water samples, graphical comparisons of major base cations and anions were made by constructing time-series graphs of concentrations by treatment. For each measured component in the water samples, annual volume-weighted lysimeter concentrations and litter leachate fluxes were calculated on a plot *x* depth combination so that one statistical test could be conducted for each depth (n=4). Post-hoc tests were performed in all cases using the LSMEANS statement in PROC GLM to evaluate the significance of mean separations with p-values adjusted by Tukey's honestly significant difference (α=0.1).

Results

Bulk soil chemistry

Compared to the forest succession (FS) soil profile, exchangeable Ca concentrations are significantly elevated from 5-200 cm in conventional tillage (CT) ($p<0.04$) and through all 200 cm in no-tillage (NT) ($p<0.03$), with the exception of the 30-50 cm layer where values under all land uses are similar (Figure 4.1; Table 4.1). Compared to FS, exchangeable K concentrations are significantly elevated from 5-100 cm in both CT ($p<0.05$) and NT ($p<0.03$) (Figure 4.1; Table 4.1). Below 5 cm, Mg concentrations are higher in CT compared to FS through 1 m, but the only significant difference is from 30-50 cm (Figure 4.1; Table 4.1). Mg concentrations are significantly elevated in NT from 5-50 cm compared to FS (Figure 4.1; Table 4.1). In contrast, FS soils have greater acidity through at least 2 m with significantly lower pH_{CaCl2} in all depth classes (Figure 4.2; Table 4.1). Exchangeable acidity in FS decreases from a peak of 1.0 $cmol_c$ kg^{-1} at 5-15 cm to 0.02 $cmol_c$ kg^{-1} from 50-200 cm with significant differences compared to CT and NT in all but the 100-150 cm depth class (Figure 4.2; Table 4.1). Below 50 cm base saturation is >98% under forest succession, whereas base saturation is >98% in the upper 50 cm in CT and NT with no measureable exchangeable acidity from 50-200 cm in the agroecosystem plots.

Full soil profile (0-2 m) exchangeable Ca and K contents and effective cation exchange capacity (ECEC) are significantly lower in the FS profile compared to the NT and CT profiles (Table 4.2). Full-profile exchangeable acidity is much greater in the FS profile but only accounts for a fraction of the difference in cation contents between the FS and agroecosystem profiles (Table 4.2). Variability in Mg concentrations from 100-200 cm masks differences in the upper

100 cm where NT and CT both have significantly greater contents compared to FS (Figure 4.1; Table 4.2).

Forest nutrient uptake

Estimated accumulation of K in forest biomass is greater than the content of this nutrient recovered in the 0-2 m exchangeable soil fraction under FS (Table 4.3). The exchangeable pool of Ca and Mg, however, exceeds that taken up in forest biomass (Table 4.3). Forest biomass accounts for <20% of Ca or Mg in the combined forest ecosystem pool (i.e., biomass and exchangeable) but ~60% of K (Table 4.3).

Litter leachate

There was a significant ($p<0.04$) separation of total cation charge in litter leachate (LL) among all the land uses with NT > FS > CT (Table 4.4). The concentrations of Ca in FS and NT LL were similar ($p=0.98$), and both were significantly higher than the Ca concentration in CT LL ($p<0.01$) (Table 4.4). The contribution of Ca to cationic charge was significantly greater in FS LL compared to NT LL ($p=0.02$) but not compared to CT LL ($p=0.45$) (Figure 4.3). Mg and K concentrations in NT LL were significantly higher compared to both CT and FS LL ($p<0.02$ for all contrasts), which were not statistically different from each other ($p>0.3$ for both Mg and K). The contribution of Mg to cationic charge was significantly greater in NT LL compared to FS and CT LL ($p=0.07$ and 0.03, respectively) (Figure 4.3). K was the dominant contributor to LL cationic charge, ranging from ~40-44% of total charge among all the LLs (Figure 4.3). LL pH was significantly lower in CT compared to FS ($p=0.07$) and NT LL ($p=0.001$) (Table 4.4). FS LL pH was also significantly lower than NT LL ($p=0.04$) (Table 4.4). Since the mean pH of all

LLs ranged from 5.9 to 6.3, the contribution of H^+ to total cationic charge was small (Figure 4.3). Together, Na, NH_4, and H contributed <8% to cationic charge in litter leachate among all three land uses (Figure 4.3). Though the absolute differences were small, Na concentrations were significantly greater in FS litter leachate compared to CT and NT (p=0.002 and 0.08, respectively) (Table 4.4).

Anionic charge in LL samples under FS and NT were predominantly due to titratable alkalinity, typically assumed to be HCO_3^- (Figure 4.4). There were significant differences among land uses for HCO_3^-, the anion deficit, and total inorganic anions, except for the contrast between NT and CT for the anion deficit (Table 4.5). Regressions of the strong acid anion deficit versus DOC, titratable alkalinity versus DOC, and the anion deficit versus DOC show good correlation between DOC and all these components (Figure 4.5). This implies that titratable alkalinity (i.e., HCO_3^-) in LL is including some organic acids with pK_a values that overlap the pH of the bicarbonate endpoint (about 4.5).

Phosphate PO_4^{3-} was the next most important component of anionic charge in NT LL with significantly higher concentrations compared to CT and FS ($p<0.0001$), whose concentrations were not significantly different (p=0.81) (Table 4.6). For FS LL, SO_4^{2-} followed organic anions as the next most important contributor to anionic charge (Figure 4.4). Both NT and FS had significantly higher SO_4^{2-} concentrations compared to CT (p=0.02 for both contrasts) (Table 4.6). Cl^- concentrations were significantly higher in CT LL compared to NT and FS (p=0.06 and 0.001, respectively) (Table 4.6) and contributed the most after titratable alkalinity to anionic charge in CT LL (Figure 4.4). There were no significant differences in NO_3 concentrations among the land uses.

Soil solution

In contrast to Ca in LL, Ca contributed significantly less to cationic charge in 15 cm soil solution under FS compared to NT and CT ($p<0.002$ for both contrasts) but not in 100 cm soil solution ($p>0.2$ for both contrasts) (Figure 4.3). Ca:Mg ratios in solution were also significantly reduced under FS at 15 cm depth compared to NT and CT ($p<0.01$ for both contrasts). Absolute Ca concentrations were more variable but also higher at both 15 and 100 cm in the agroecosystem plots compared to FS (Figure 4.6; Table 4.4). At 15 and 100 cm depth, differences were significant between FS and CT ($p=0.09$ and 0.08, respectively) but not between FS and NT ($p=0.29$ and 0.11, respectively). Although total cationic charge was elevated at both 15 and 100 cm under CT and NT compared to FS, the differences were not significant at 15 cm ($p=0.12$ and 0.46, respectively) (Table 4.4). At 100 cm, total cationic charge was different between FS and CT ($p=0.08$) but not between FS and NT ($p=0.12$). Mg and K concentrations also tended to be elevated in CT and NT plots at both depths (Figure 4.7 and 4.8). Differences in Mg and K concentrations at 15 cm were not significant among the land uses ($p>0.24$ for all contrasts). At 100 cm in the CT plots, Mg concentrations were significantly higher compared to FS ($p=0.08$) but not compared to NT ($p=0.96$) (Table 4.4). K concentrations at this depth were also elevated in the CT plots compared to both NT and FS ($p=0.07$ and 0.04, respectively) (Table 4.4). Although K only contributed 3% to total cationic charge in 100 cm CT soil solution, this was significantly higher than the contribution of K to total cationic charge at this depth under NT (1.2%) ($p=0.08$). Similar to litter leachate, Na concentrations were consistently elevated in FS soil at both depths compared to NT and CT (Figure 4.9). The differences were significant at 15 and 100 cm compared to NT ($p=0.03$ and 0.01, respectively) and at 100 cm compared to CT ($p=0.04$) (Table 4.4). Na also contributed significantly more to cationic charge at 15 and 100 cm depth under FS compared to the agroecosystem plots ($p<0.01$ for all contrasts) (Figure 4.3). Finally, in contrast to results obtained from soil sampling, there were no significant differences in soil solution pH at 15 and 100 cm ($p>0.17$ for all contrasts), although FS soil solution was more acidic at both depths (Table 4.4). Like LL, the contribution of H^+ to cationic charge in soil solution was negligible among all land uses (Figure 4.3; Table 4.4).

In contrast to LL, mean NO_3^- concentrations were consistently elevated in soil water in CT and NT (Figure 4.10). Annual volume-weighed NO_3 means were an order of magnitude greater than those in FS (Table 4.6). Compared to FS, HCO_3^- was also consistently elevated at 100 cm under NT and at both depths under CT (Figure 4.11).

Wide variability in soil solution concentrations of NO_3 (CVs > 100% for all depth by land use combinations) and of HCO_3^- (CV's 33-145% for all depth by land use combinations) made mean separations among the land uses for these components statistically non-significant ($p>0.35$ for all contrasts) (Table 4.6). An ANCOVA analysis of the agroecosystem plots with total volume collected from each lysimeter as a covariate revealed a winter crop effect on NO_3^- concentrations ($p=0.09$) in the overall model with higher concentrations under N-fixing clover compared to rye. The winter crop effect, however, was not significant when analyzed separately by either depth. Neither depth nor tillage treatment had a significant effect on NO_3 concentrations in the overall model ($p=0.9$ and 0.6, respectively).

There was less variability in total anion concentrations in soil water (Table 4.6), because HCO_3^- and NO_3^-, the dominant anions in agroecosystem soil water, are inversely related (Figure 4.12). Under FS, SO_4^{2-} and Cl^- make up a significantly greater proportion of total anionic charge at both 15 and 100 cm ($p<0.08$ for all contrasts; Figure 4.4). FS Cl^- concentrations were significantly higher at 100 cm compared to both CT and NT ($p<0.01$) but not at 15 cm ($p>0.13$

for both contrasts) (Table 4.6). There were no significant differences in SO_4^{2-} concentrations at either 15 or 100 cm depth ($p>0.35$ for all contrasts; Table 4.6).

In these mineral soil solutions there is a negative correlation between DOC and the strong acid anion deficit and between DOC and titratable alkalinity (Figure 4.13). Therefore, in mineral soil solution, titratable alkalinity is likely an acceptable measure of HCO_3^-.

Hydrologic Fluxes

Precipitation during the year-long monitoring period was 76% of the long-term (1978-2007) average and estimated fluxes at 15 and 100 cm depth were also below normal (Table 4.7). Fluxes predicted by the different PET methods differed by 10 cm yr^{-1} at 15 cm depth (Table 4.7), and predicted lysimeter collections match actual collections reasonably well (Figure 4.14). The Penman-Monteith appeared to do a better job in predicting a rapid dry down towards the end of April, because the number of lysimeters making collections began to drop at this date (Figure 4.14). This accompanied the leafing-out of the forest and rapid growth of plants in the agroecosystem plots in mid-April. However, the Penman-Monteith short-term model predicted no lysimeter collections at 100 cm (Figure 4.14). Using the PET estimate from Penman-Monteith, the long-term average flux at 100 cm was 33% that predicted by Thornthwaite (Table 4.7). This was due to much higher PET estimates from November-May but not during the hotter summer months (data not shown). On the other hand, the Thornthwaite method predicted lysimeter collections thru June 2008, while only 1-3 lysimeters collected water from the end of May 2008 thru July 2008 at 100 cm (Figure 4.14). Since monthly precipitation data is divided evenly among time-steps in the long-term model, fluxes are slightly dampened. This is apparent from the calculated fluxes at 15 cm and 100 cm during 2007-2008. The long-term model estimates for the 2007-2008 period are 10-20% less than those calculated using daily precipitation data (Table 4.7). Finally, since previously published leaching rates from HSB were based upon use of the Thornthwaite calculation method for PET (Stinner et al., 1984), the Thornthwaite method was also used to estimate the 2007-2008 leaching rates for the purpose of historical comparison (Table 4.8).

Discussion

Soil acidification

Although results from the beginning of the HSB experiment suggested no-till (NT) agriculture may more efficiently cycle nutrients compared to conventional tillage (CT) (Stinner et al., 1984), the current 0-2 m soil exchangeable contents of Ca, Mg, and K under CT and NT does not provide strong evidence in support of this hypothesis (Table 4.2). Current solution monitoring suggest leaching may be slightly enhanced under CT at 15 cm but not significantly (Tables 4.4 and 4.8). The major contrast that emerged from this study is not between CT and NT but between the forest succession (FS) and the agroecosystem soil profiles. The remaining discussion will be devoted to this contrast.

Ideally, soils under all three land uses would have been sampled to a depth of 2 m before the agroecosystem experiment began in 1978. Unfortunately, only data from the 0-10 cm layer is available from an April 1980 sampling just before the May 1980 liming of the agroecosystem plots. These data showed similar levels of exchangeable Mg and Ca under both the land undergoing natural succession at HSB and the agroecosystem plots: 348, 335, and 328 μg Ca g^{-1} and 38.1, 34.2, and 32.3 μg Mg g^{-1} soil for FS, NT, and CT, respectively (Stinner et al., 1984). Higher exchangeable K in the agroecosystem during this sampling was attributed to 240 kg ha^{-1}

of K in fertilizer applied for two years prior to the sampling. While the early successional areas sampled in 1980 were not the exact same areas sampled for the present work, this historical sampling suggests that initial base saturation levels were likely similar across the alluvial terrace at HSB with the exception of inherently variable Mg^{2+} concentrations below 1 m (Figure 4.1).

Accepting a somewhat similar starting condition, then three decades of forest succession (FS) in the absence of fertilization has resulted in significantly lower exchangeable base cations and soil pH and significantly greater exchangeable acidity through at least 2 m depth (Figures 4.1 and 4.2; Table 4.2) relative to CT and NT.

Overall, the relative soil acid status under FS has three possible mechanisms: first, CT and NT may simply reflect the effects of the base cation additions through fertilizer penetrating to at least 2 meters; second, cation leaching under FS may have been greater at some point in the past three decades due to higher anion production (organic acid, HCO_3^-, or NO_3^-); and third, FS has led to a large transfer of base cations relative to anions from soil to vegetation. In reference to the first mechanism, the 57 $kmol_c$ CO_3^{2-} contained in the lime applied to the agroecosystem plots represents a H^+ neutralization capacity that is greater than the current full-profile exchangeable acidity content of 42 $kmol_c\,ha^{-1}$ under FS (Table 4.2). This suggests that liming the agroecosystem plots could neutralize or alkalinize all the acidity in the profiles. The lack of any exchangeable acidity in CT or NT profiles is surprising, however, since no additional lime has been applied since 1980. Furthermore, mass balance accounting of these base inputs relative to FS, as discussed further below, indicates that acidification processes have been active over this period.

The mass balance for the exchangeable Mg content difference (0-1 m) and the exchangeable K content difference (0-2 m) between the CT-NT average and FS can be explained by applications of fertilizer (Table 4.2). In other words, the observed difference is less than fertilizer inputs. However, due to the large quantity of forest biomass, inclusion of base cation uptake in the mass balance represents a large pool of Ca, Mg, and K relative to the exchangeable contents in the full soil profile (0-2 m) (Table 4.3). When the FS uptake of these nutrients is included, the exchangeable pools of K and Mg in the agroecosystem soil profile should still be substantially greater than the combined FS exchangeable pool and FS uptake. For example, in the case of K, the biomass uptake exceeds the observed difference in CT-NT versus FS. This means the fertilizer K applied to the agroecosystem is essentially missing (Table 4.3). Although the Mg uptake does not exceed the exchangeable Mg difference, the excess exchangeable Mg in CT-NT is almost four times smaller than the Mg fertilizer application (Table 4.3). The mass balance in Ca contents between the agroecosystem soil profile and forest ecosystem are quite different from those of K and Mg. The difference in Ca greatly exceeds the amount of fertilizer applied and suggests an unaccounted for removal of Ca in FS (Table 4.3).

The second mechanism proposed is differences in leaching under the land uses. Can leaching explain the failure to account for differences in Mg, K, and Ca? Past and current measurements of HSB soil solution components suggest that base cation leaching has been greater under the agroecosystem and thus might explain the missing K and Mg applied in fertilizer. Similar to the current estimated annual leaching fluxes (Table 4.8), fluxes of Ca, Mg, and K through leaching in the agroecosystem were at least twice as high as those under forest succession at the beginning of the experiment (Stinner et al., 1984). Overall, their estimated nutrient fluxes through leaching were 2-5 times greater than current estimates from August 2007 to July 2008, which is partially explained by greater water fluxes during their monitoring period (Table 4.7). If these elements are leached below rooting depth, then the unaccounted for Mg in fertilizer (Table 4.3, approximately 18.4 $\mathrm{kmol_c\ ha^{-1}}$ from 0-100 cm) would amount to an increase in leaching of 0.6 $\mathrm{kmol_c\ ha^{-1}\ yr^{-1}}$ under CT and NT. While this appears to have been possible from 1979-1980, such a difference in leaching is not seen in the 2007-2008 data, even at the shallower depth of 15 cm (Table 4.8). If all of the fertilizer K leached out of the agroecosystem profiles (27 $\mathrm{kmol_c\ ha^{-1}}$), this would amount to a leaching rate of 0.9 $\mathrm{kmol_c}$ K or 35 kg K $\mathrm{ha^{-1}\ yr^{-1}}$ over the course of 30 years, which is greater than any estimated K leaching rate at HSB (Table 4.8).

While earlier and current solution monitoring suggests that cation leaching has been lower under FS, no solution monitoring occurred from 1980 to 2007. The question then becomes: could base cation leaching possibly have been greater during this period under FS? Of course, if this scenario of elevated leaching under FS were true, this would further complicate the K and Mg accounting, because leaching rates of base cations should co-vary.

Two major factors control base cation equilibrium concentrations in soil solution, base saturation and concentrations of anions in solution (Cosby et al., 2001). Exchangeable acidity data from 2007 show that the cation exchange complex on the CT and NT profiles is nearly 100% saturated with base cations (Ca, Mg, and K), since there was only a small amount of exchangeable acidity in the 0-15 cm depth classes, whereas base saturation in the FS profile is as low as 57% from 5-15 cm but is >98% from 50-200 cm (Figure 4.2). As base saturation decreases, base cations contribute less to total cationic charge in solution, as described mathematically with the Gaines-Thomas or Gapon expressions. Thus, decreasing base saturation at 15 cm under forest succession would have the effect of actually decreasing base cation fluxes through 15 cm depth with percolating water. However, during the past 30 years, the dynamic role of base saturation on equilibrium chemistry has probably been of less importance at 100 cm depth, since base saturation is still currently >98% at 100 cm under all three land uses.

Changing anion concentrations from 1980-2007 could have also affected cation leaching rates. The NT litter leachate (LL) had a significantly higher strong acid anion deficit compared to FS. This suggests that organic acids under HSB forest succession are not inducing greater cation transport with percolating LL relative to the NT system. The higher anion deficit in FS LL (Table 4.5), which is the conventional estimation of the charge from organic anions (Cronan et al., 1978), probably reflects a higher concentration of organic anions with lower pK_a values, that is, those organic species not yet protonated by added acid at pH 4 during the gran-titration. Deeper in the soil profile, the anion deficit represents a significantly greater proportion of anionic charge in FS soil solution, particularly compared to CT.

Relative to the anion deficit in soil solution, contributions of NO_3 and HCO_3 to anionic charge are greater among all three land uses (Figure 4.4). Thus, varying concentrations of HCO_3 and NO_3 have probably been more important than organic anions in controlling losses of cations due to leaching from the soil profile. Indeed, the Ca concentrations reported by Stinner et al. (1984) appear correlated to NO_3-N concentrations in solution (Table 4.9). Higher NO_3^- leaching in the agroecosystem plots was probably due to 260 kg N ha^{-1} of fertilizer applied to the agroecosystem plots from May 1978 to November 1979. Total application of 1200 kg N ha^{-1} to the rye split plots and 760 kg N ha^{-1} to the clover split plots over the course of the agroecosystem experiment would therefore be expected to enhance base cation leaching in the CT and NT profiles compared to the FS profile. Although N fertilizer has not been applied since 1999, high NO_3^- concentrations were still observed in half the lysimeters installed in the agroecosystem plots during 2007-2008. Analysis of agroecosystem lysimeters with respect to the winter cover split-plot in which they were installed suggests that high NO_3 hot-spots in the agroecosystem plots are mostly related to clover N-fixation. Thus, although more than 75% of the N fertilizer was applied before 1992, the mean effect of NO_3^- concentrations on cation leaching in the CT and NT treatments would still be expected to have been greater compared to FS particularly under the clover split plot.

The other anion to consider is HCO_3^-. In the agroecosystem lysimeters with low NO_3^- concentrations, high HCO_3^- concentrations were usually observed (Figure 4.12). The dissociation of H_2CO_3 into H^+ and HCO_3^- is determined by soil water pH, while the absolute concentration of dissolved H_2CO_3 in soil water is determined by the partial pressure of carbon dioxide (pCO_2). Essentially, H_2CO_3 is favored over HCO_3^- at lower soil pH, meaning less alkalinity can be generated at a lower soil pH, given the same soil $pCO_{2.}$ Since the nitrification reaction results in a net release of protons, this explains why generation of alkalinity would tend to be depressed in nitrification hot-spots.

Deductions about concentrations of HCO_3^- can be made from earlier solution sampling (Stinner et al., 1984). Subtraction of the charge due to NO_3 from the sum of measured cations reveals a greater anion charge deficit under CT and NT compared to FS (Table 4.9). Other balancing anions, of course, may include SO_4 (Table 4.6), Cl^- (Table 4.6), organic anions (Figure 4.4) or HCO_3^- (Table 4.9). Only in the case of HCO_3^- can a mechanism for increased concentrations be supported. Shortly after initial cultivation in CT higher soil pCO_2 from enhanced soil respiration would be expected. Assuming no difference in soil pH at 60 cm depth during these earlier solution samples, then the higher pCO_2 would contribute higher HCO_3^- concentrations. In the case of the relatively high pH soils at HSB, high pCO_2 leads to a corresponding high level of alkalinity.

Nevertheless, since a lower soil pH under FS is currently observed, this confounds the ability to interpret currently observed, lower levels of alkalinity as lower soil pCO_2 under FS. Measurements of soil CO_2 efflux at HSB during the cool season of 1983-1984, which is when most leaching occurs, revealed similar rates that were not statistically different among the old-field in succession, older forest near the river, and the agroecosystem treatments, although efflux rates were consistently higher from NT plots (Hendrix et al., 1988). Summer 1984 efflux rates as high as 50 g CO_2 m^{-2} in the agroecosystem rose well above the peak efflux rates of 10 g CO_2 m^{-2} in the old-field and forest at HSB (Hendrix et al., 1988). Unpublished data from the early 1990s also showed significantly lower median CO_2 efflux rates from areas of forest succession at HSB compared to the agroecosystem plots (Burke et al., 1997). These efflux measurements of CO_2 out of the soil profile all suggest that soil pCO_2 levels were not greater in the forest succession profile during the period in which no soil solution monitoring occurred (1980-2007). As such, there is little evidence to support greater HCO_3^- and NO_3^- concentrations in the FS profile or greater cation, or specifically Ca, leaching rates during the past 30 years.

The third mechanism, base cation uptake in forest biomass may well be the primary mechanism of soil Ca depletion under forest succession (Table 4.2). The forest LL at HSB reflects the high base saturation of the soil, so that acidic, incoming rain with 20 be H^+ L^{-1} has protons rapidly exchanged with Ca, Mg, K, and Na. The fact that the forest LL is significantly enriched in Ca^{2+} compared to the CT LL and not significantly different compared to the NT LL probably reflects the impressive uptake and storage of Ca^{2+} by the HSB forest during the past thirty years (Table 4.4).

An early study that compared old-field, herbaceous vegetation at Horseshoe Bend after 12 years of succession with agroecosystem vegetation measured 7500 μg g^{-1} Ca in old-field biomass. Similar levels were found in the weeds of CT and NT plots (7500-8600 μg g^{-1} Ca) but less in sorghum and rye (2100-3900 μg g^{-1} Ca) (Stinner et al., 1983). The current estimate of Ca uptake into forest biomass has an average concentration of 4060 μg g^{-1}. Since Ca content regressions came from work in the coastal plain of GA, it is likely that the uptake of Ca has been underestimated. If tree biomass has a concentration of 7500 μg g^{-1} Ca and if root biomass was included in the estimate, this would probably account for most of the missing Ca in Table 4.3.

Finally, the calculation in Table 4.3, however, does neglect annual uptake of base cations by plants in the agroecosystem plots, which would have been missed in the 2007-2008 sampling efforts. Previous work at HSB estimated annual uptake of 2.2 ± 0.3, 2.4 ± 0.7, and 4.4 ± 1.2 $kmol_c$ ha^{-1} yr^{-1} for Ca, Mg, and K, respectively, in the agroecosystem plots (means ± 1 SD, n=3 years) (Stinner et al., 1984). This suggests that annual uptake of K would represent the only appreciable proportion of whole profile exchangeable cations but not nearly enough to account for the missing fertilizer input of K (Table 4.3).

Litter leachate estimates show nearly 100 kg K ha yr^{-1} being cycled in the NT system and 60 kg K ha yr^{-1} being cycled in the FS system. Another possible mechanism for the K fertilizer not recovered in the exchangeable fraction in the agroecosystem plots, which would also help explain the lack of increase in total soil N in the agroecosystem plots in spite of N fertilization and fixation (Chapter 3), is nutrient export by white-tailed deer that have frequently been seen grazing the agroecosystem plots (personal observation). The deer may be consuming and transferring K rich biomass out of the agroecosystem that annually accumulates 4-5 $kmol_c$ K ha^{-1} in aboveground biomass. This hypothesis has been suggested as an important biogeochemical mechanism for nutrient transfer in an agricultural-forest landscape mosaic (Seagle, 2003) and is worthy of further investigation.

Conclusions

Thirty years of forest succession alongside an agroecosystem experiment comparing no-till and conventional till agriculture have produced soil profiles with significantly different levels of exchangeable base cations and acidity. The significant contrast that emerged was between the forest succession soil profile and the agroecosystem—not between the conventional tillage and no-till treatments. A mass balance approach combined with a review of data collected during the course of the experiment gave insight into but not a complete explanation of the mechanisms that produced these changes.

Applications of fertilizer to the agroecosystem can explain significantly elevated levels of Mg and K but not significantly elevated levels of Ca in the agroecosystem soil profile. The exchangeable acidity in the forest succession profile could also be explained by neutralization capacity of lime applied to the agroecosystem plots. When substantial uptake of base cations by the rapidly growing forest is added to the forest soil exchangeable pool, then the difference in Mg and K between the agroecosystem and forest is exceeded by applications of fertilizer to the agroecosystem. This suggests leaching loss in the agroecosystem of applied Mg and K, which is conceptually supported by solution sampling done at the beginning of the experiment and in the present work. However, the specific leaching rates needed to explain the missing fertilizer Mg and K are not supported by the calculated differences in leaching rates. High spatial variability of exchangeable Mg from 1-2 m depth also complicated a full-profile accounting of changes in Mg that had occurred during the past 30 years due to land use.

In the case of Ca, current estimates of forest uptake and lack of fertilizer application do not completely account for the lower content of exchangeable Ca under FS. Like Mg and K, Ca leaching rates were also higher in the agroecosystem at the beginning of the experiment. Non-significant but higher rates of Ca leaching were also observed in the present work in the agroecosystem. Although no solution monitoring occurred from 1980 to 2007, consideration of the law of charge balance suggests that leaching would have still been higher under CT and NT. Applied fertilizer N and nitrogen fixation by a winter cover crop probably continued to drive production of NO_3^- and higher soil CO_2 combined with lower levels of soil acidity probably drove higher generation of HCO_3. Given the law of charge balance and the fact that base saturation is still >98% below 50 cm under all three land uses, then these higher concentrations of anions in solution in the agroecosystem would have generated greater base cation leaching. Organic anions were found to be a minor component of anionic charge in soil solutions, though they may be significantly elevated under forest succession. Greater forest uptake of Ca^{2+} than what is currently estimated may account for the observed difference. Clearly, processes of acidification have been operating under both forest and agro-ecosystem but by different mechanisms.

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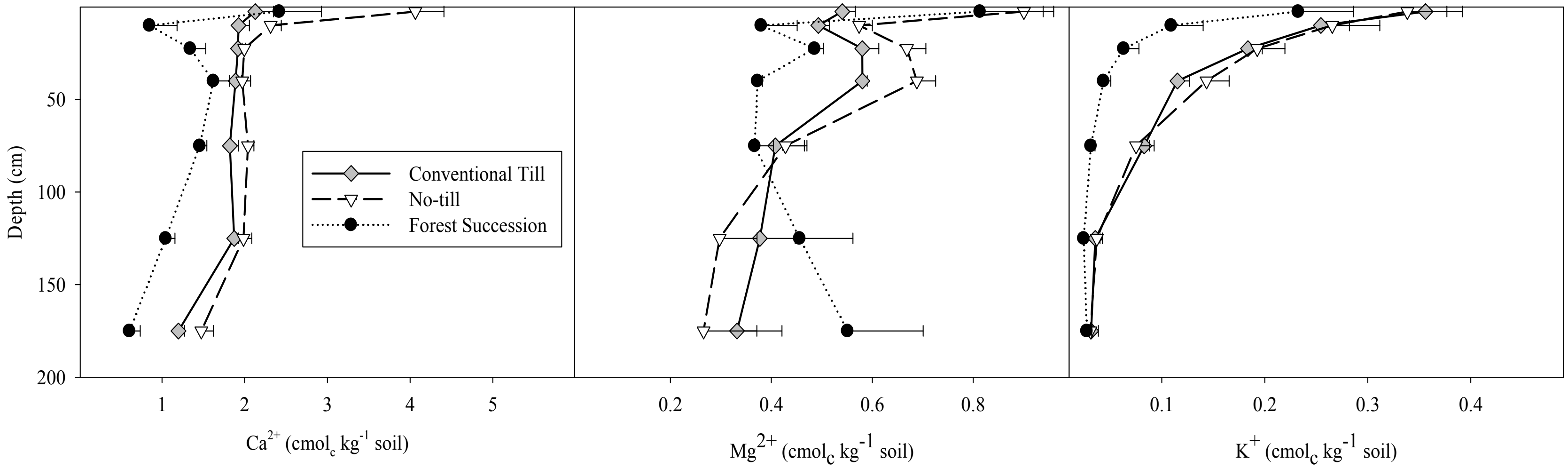


Fig 4.1. Cation exchange chemistry (means ± 1 SE) for a Typic Kanhapludalf under the Horseshoe Bend Agroecosystem Experiment (n=4), Athens, GA, USA, March 2007.

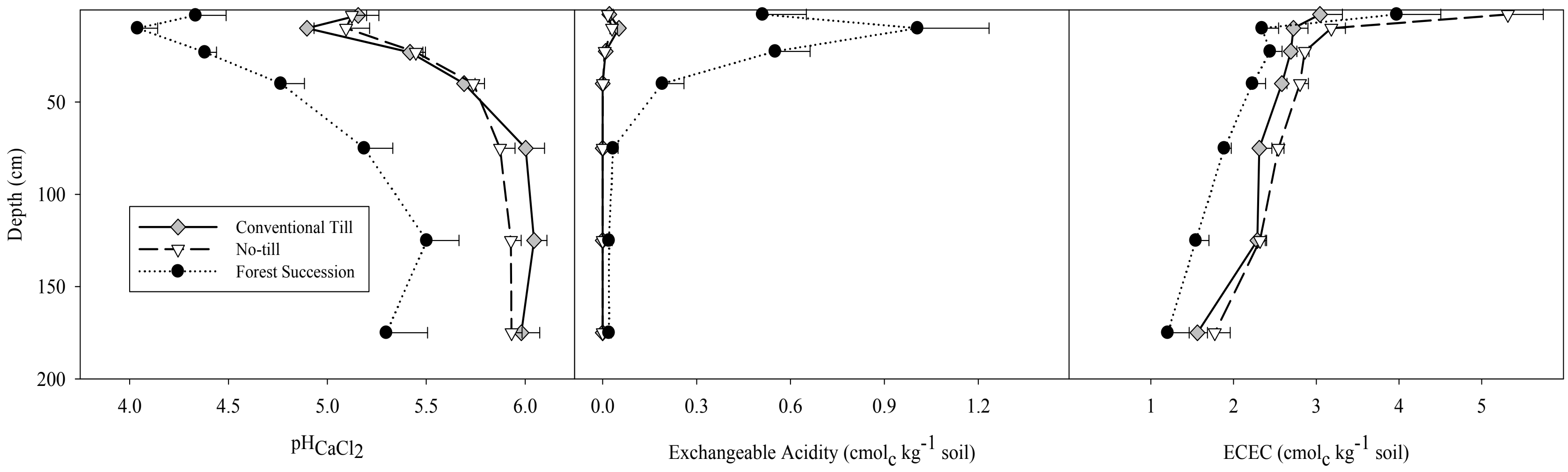


Fig 4.2. Soil acidity and effective cation exchange capacity (ECEC) (means ± 1 SE) for a Typic Kanhapludalf under the Horseshoe Bend Agroecosystem Experiment (n=4), Athens, GA, USA, March 2007.

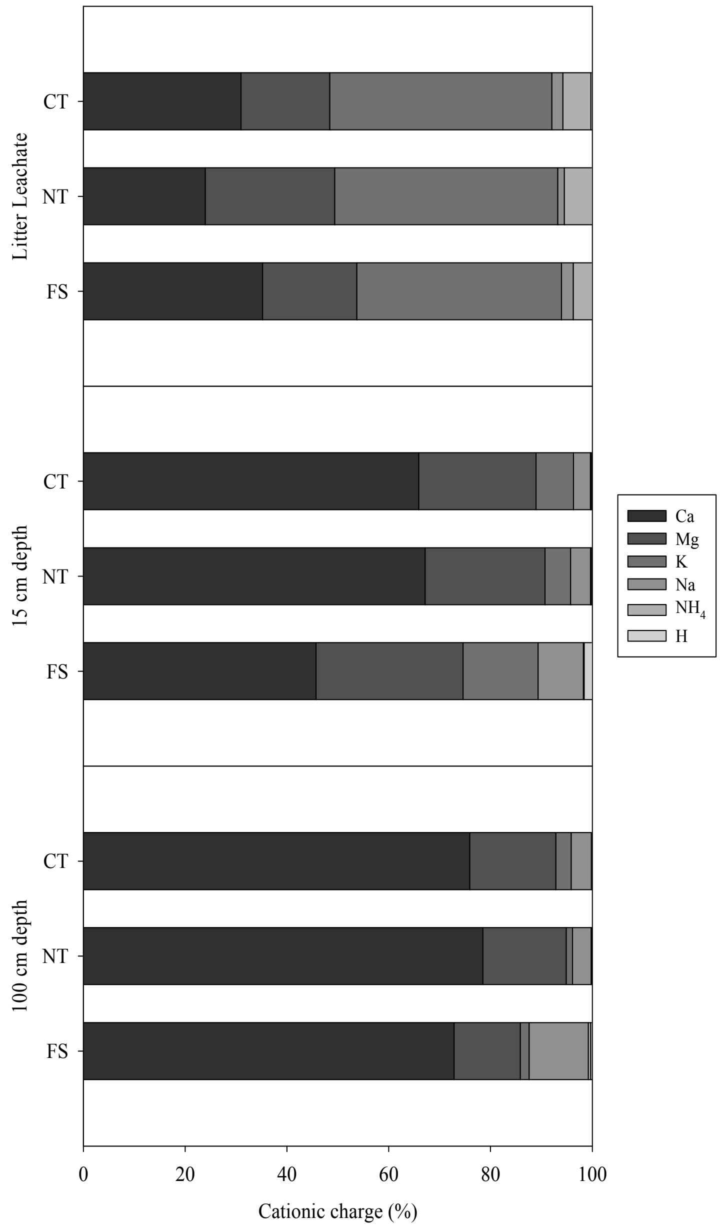


Figure 4.3. Individual cation contributions to total cationic charge. The proportions are derived from nine month, volume-weighted means by plot for each depth (n=4) from Nov-Jul-2008 at Horseshoe Bend, Athens, GA, USA. NH_4 comprises <1% of cationic charge in soil solution, whereas H^+ only comprises >1% of cationic charge in forest soil solution at 15 cm depth. CT=conventional till; NT=no-till; FS=42-yr-old Forest Succession.

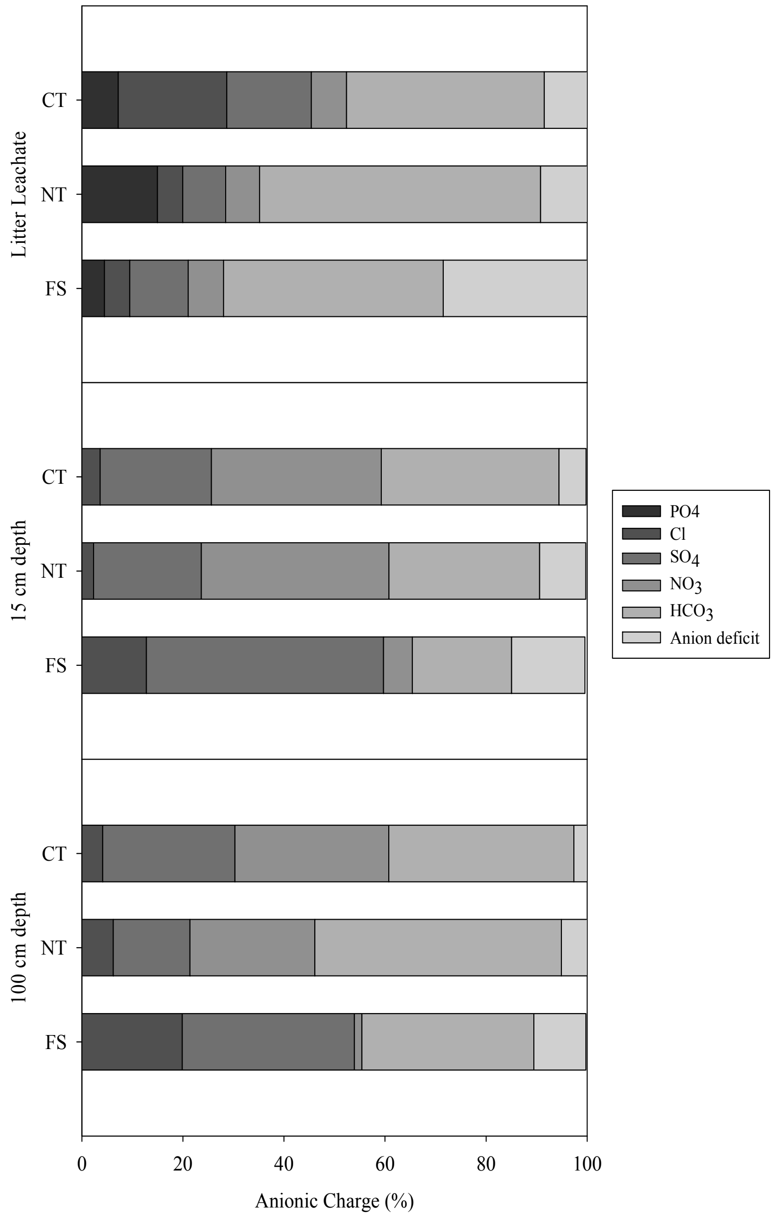


Figure 4.4. Individual anion contribution to total anionic charge. The figure is derived from seven month, volume-weighted means by plot for each depth (n=4) from Jan-Jul 2008 at Horseshoe Bend, Athens, GA, USA. The contribution of PO_4 to anion charge in soil solution is <1%. CT=conventional till; NT=no-till; FS=42-yr-old Forest Succession.

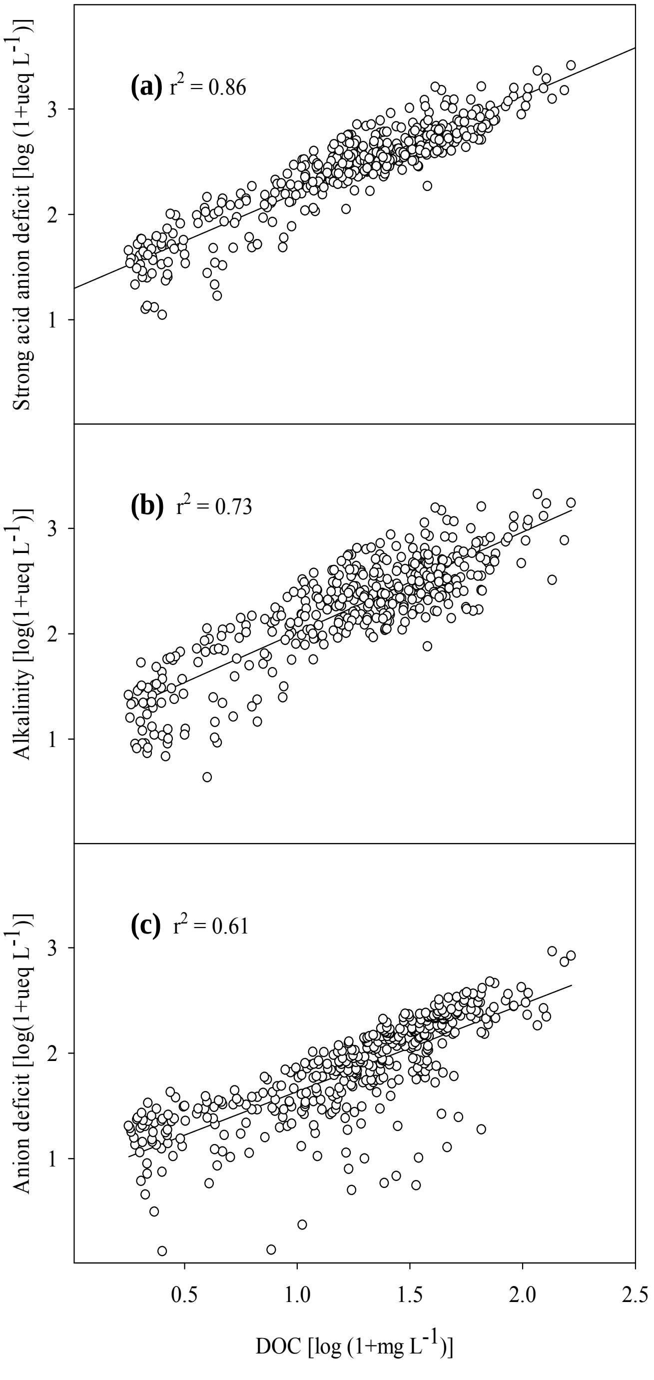


Figure 4.5. Relationships between dissolved organic carbon (DOC) in litter leachate samples and (a) strong acid anion deficit (b) titratable alkalinity and (c) anion deficit. Anion deficit and strong acid anion deficit are estimated by charge balance including or excluding HCO_3, respectively. Thirty-three samples with negative anion deficit estimates were excluded from January-July 2008 samples collected under three land use types (conventional till, no-till, or forest succession at the Horseshoe Bend Agroecosystem Experiment, Athens, GA, USA (n=407).

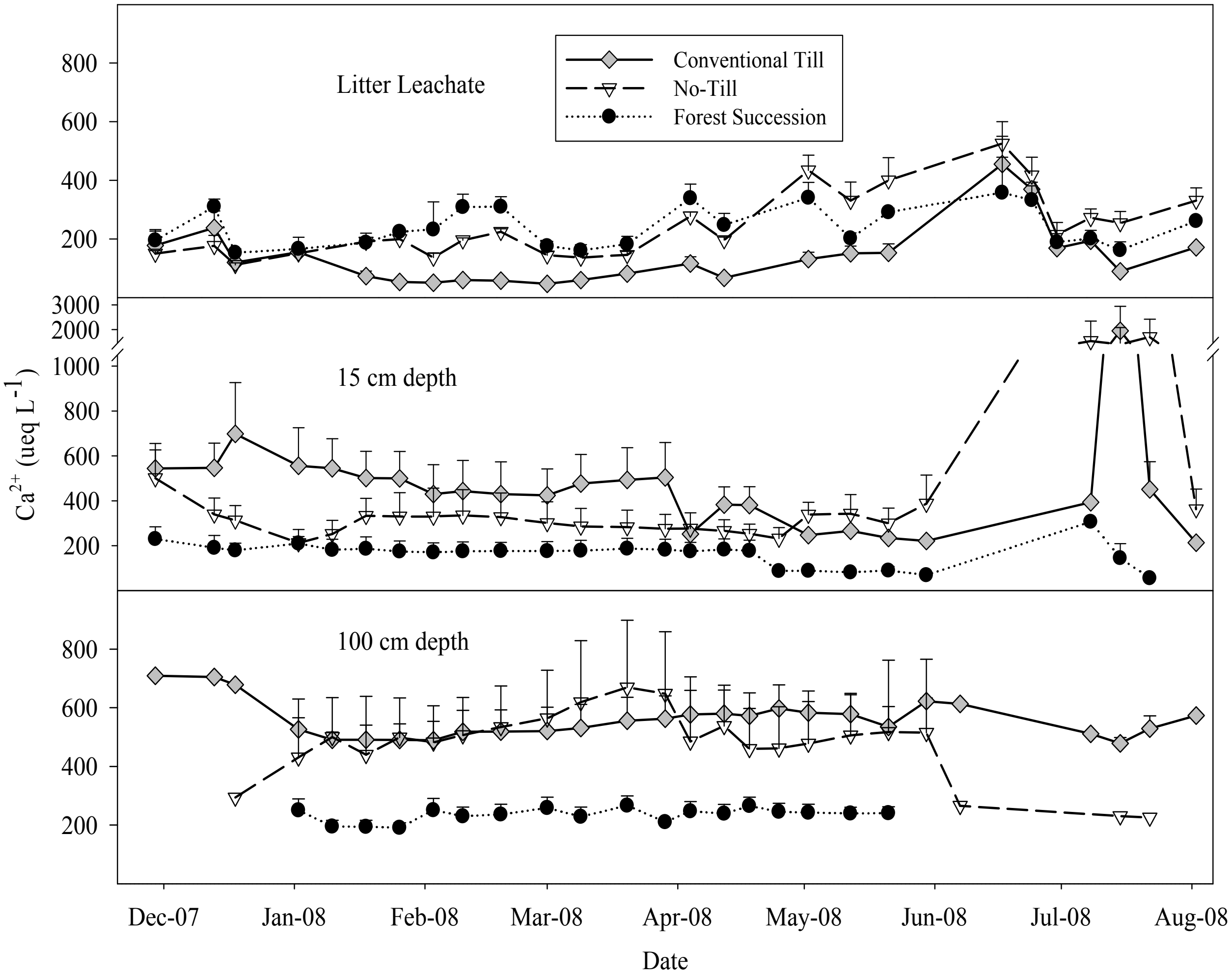


Figure 4.6. Calcium concentrations in soil solutions (means ± 1 SE) at Horseshoe Bend Agroecosystem experiment (n=4), Athens, GA, USA.

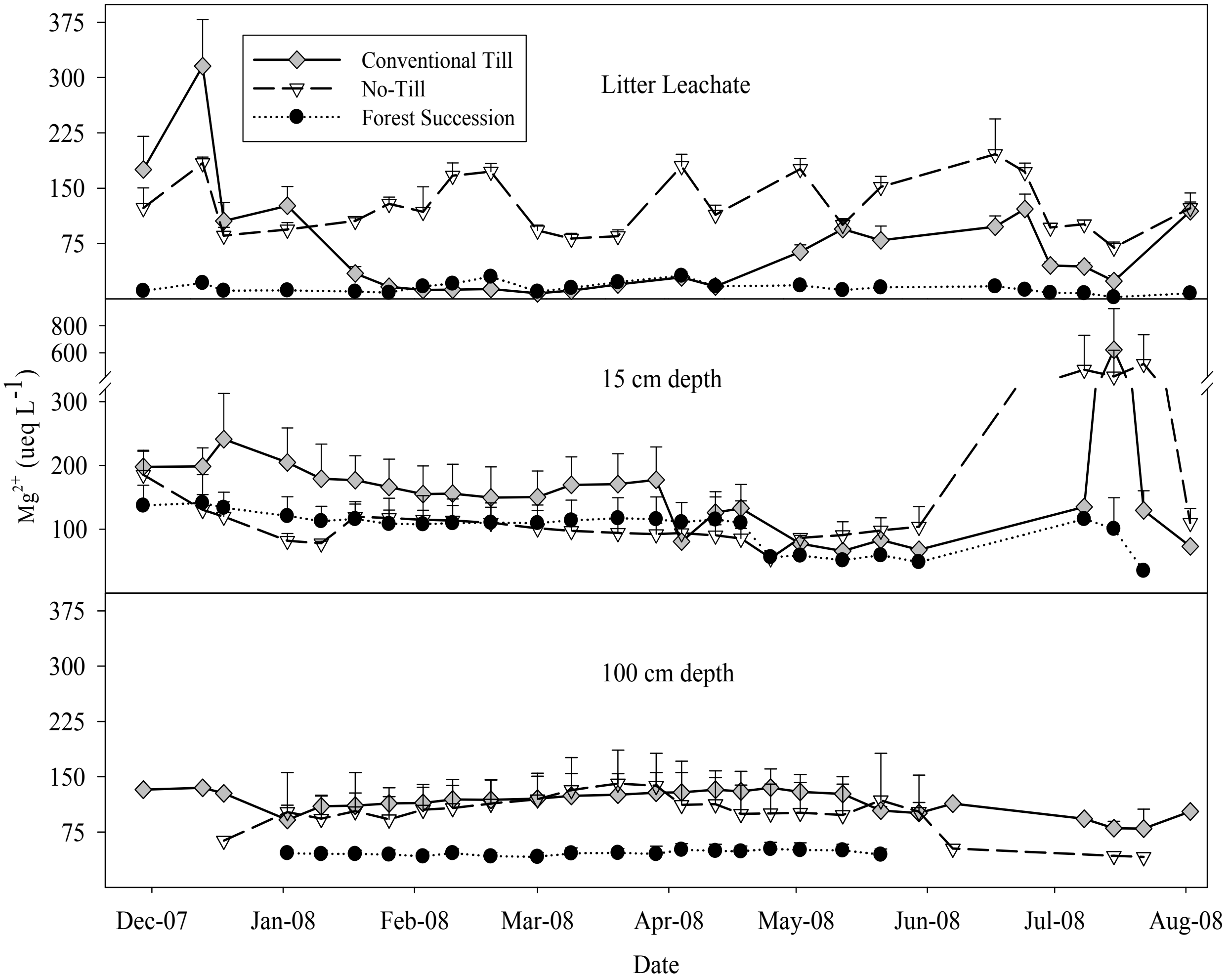


Figure 4.7. Magnesium concentrations in soil solutions (means ± 1 SE) at Horseshoe Bend Agroecosystem Experiment (n=4), Athens, GA, USA.

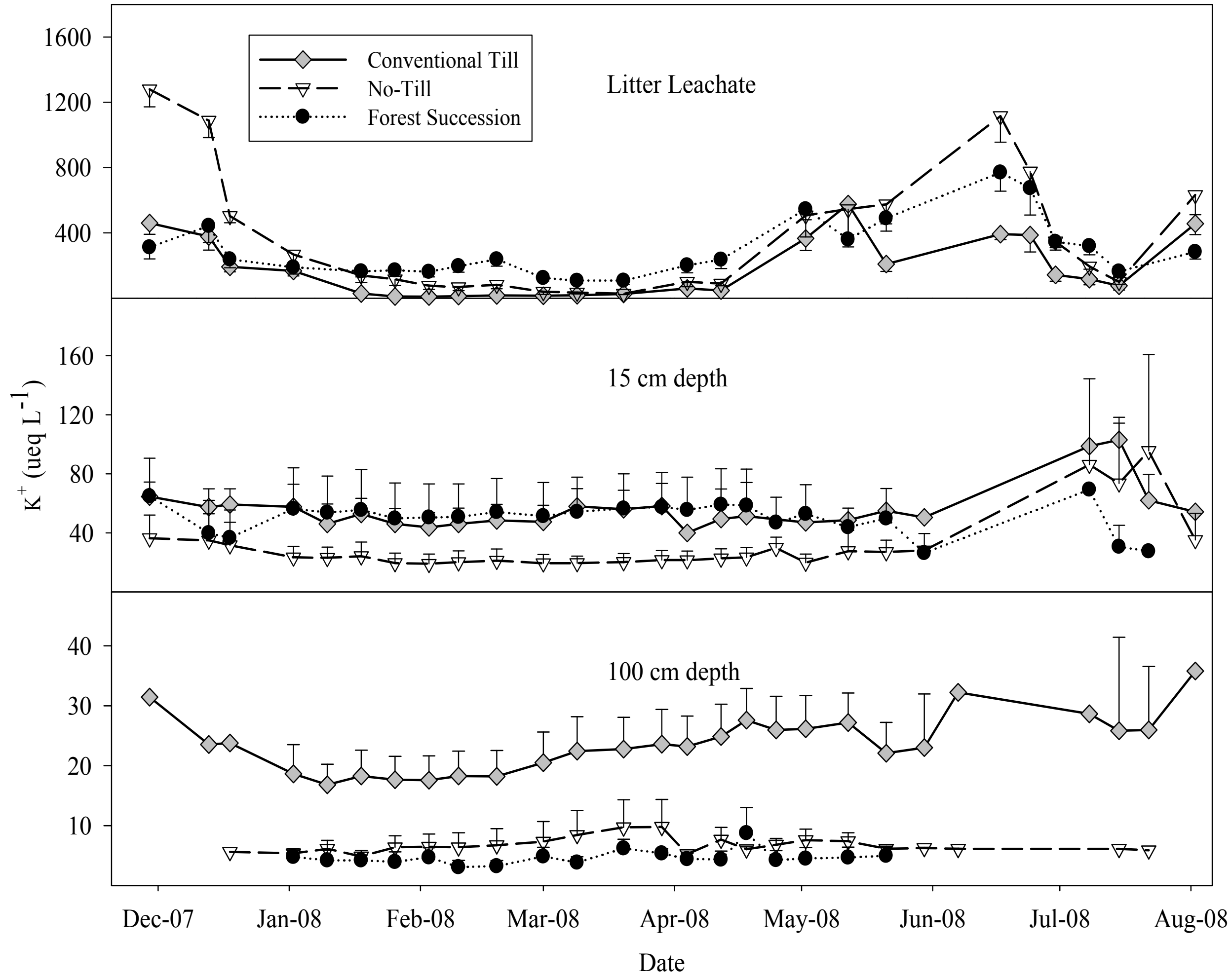


Figure 4.8. Potassium concentrations in soil solutions (means ± 1 SE) at Horseshoe Bend Agroecosystem experiment (n=4), Athens, GA, USA.

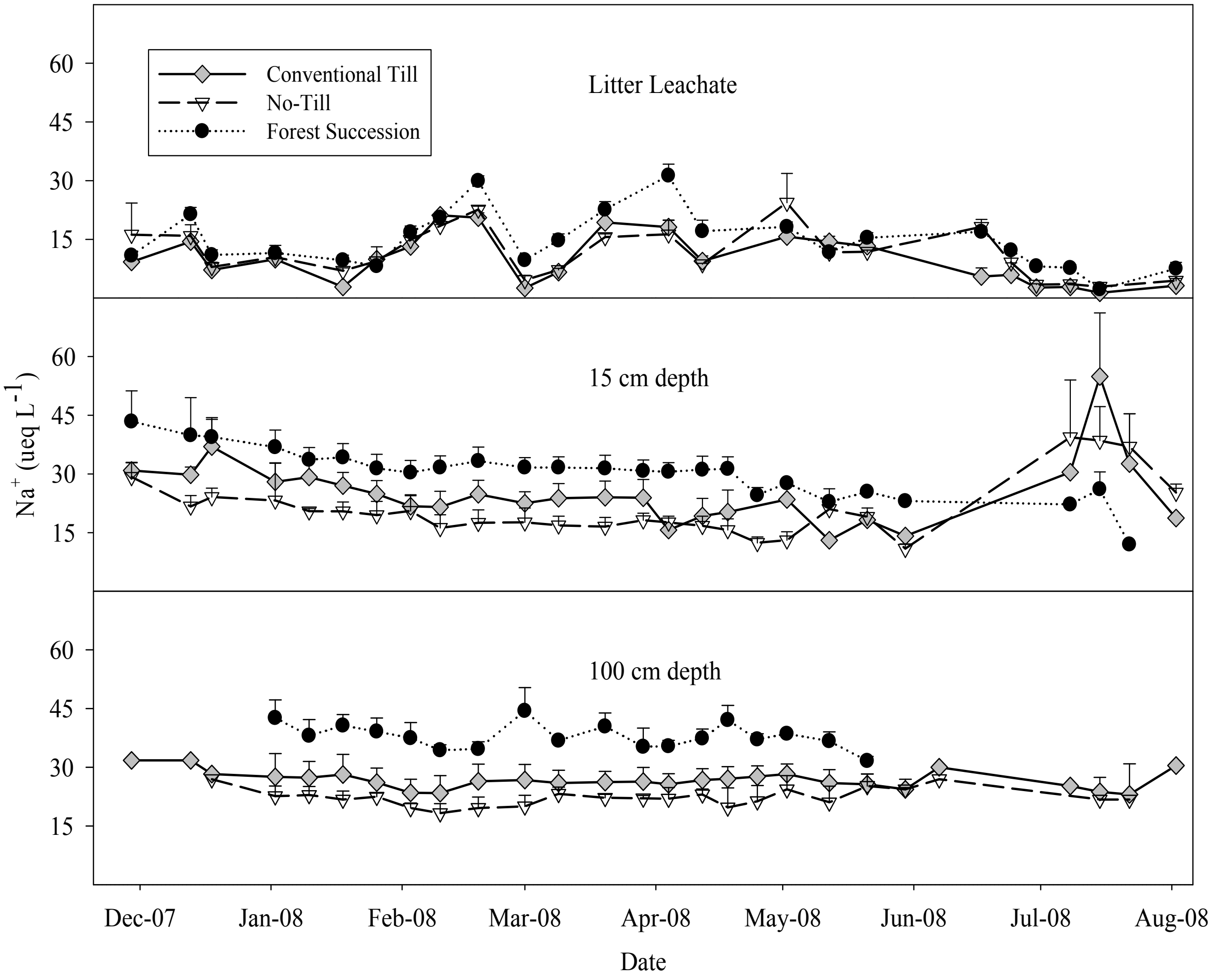


Figure 4.9. Sodium concentrations in soil solutions (means ± 1 SE) at Horseshoe Bend Agroecosystem experiment (n=4), Athens, GA, USA.

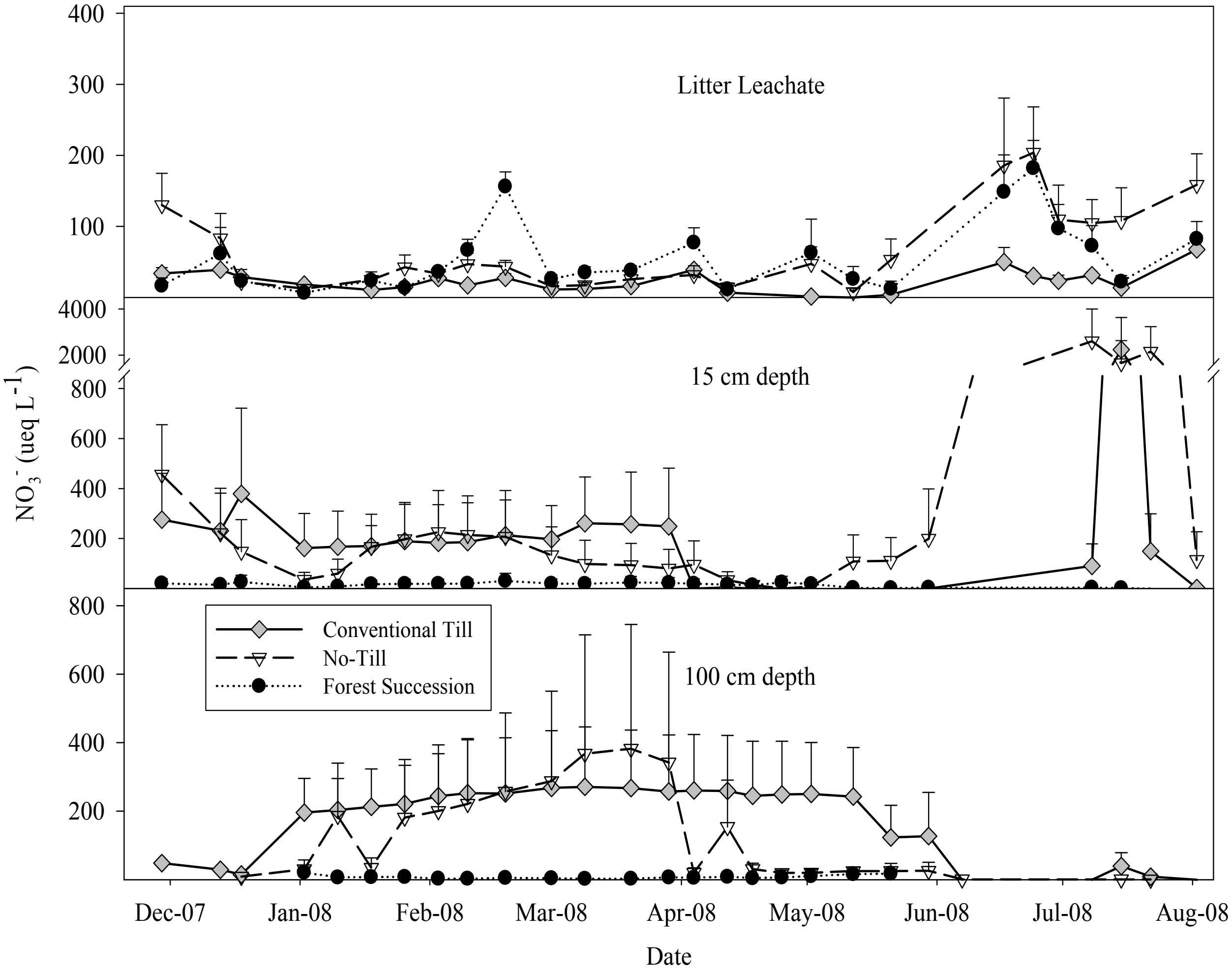


Figure 4.10. Nitrate concentrations in soil solutions (means ± 1 SE) at Horseshoe Bend Agroecosystem experiment (n=4), Athens, GA, USA.

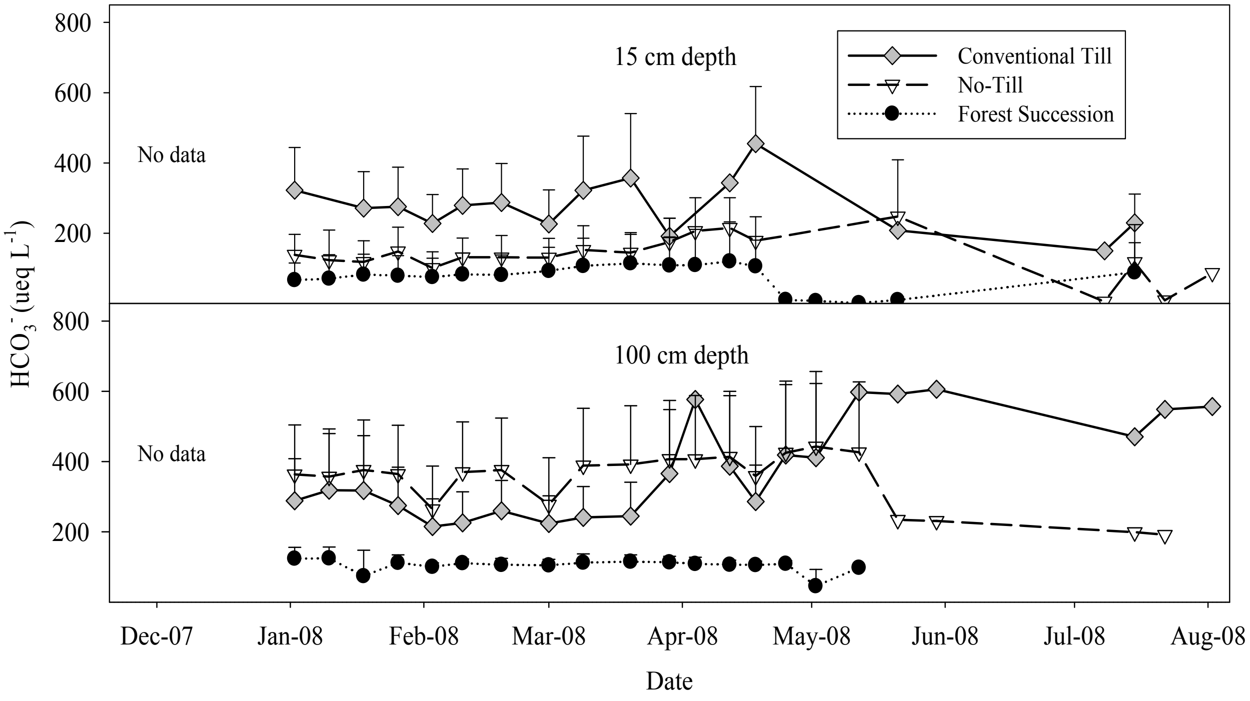


Figure 4.11. Bicarbonate (titratable alkalinity) concentrations in soil solutions (means ± 1 SE) at Horseshoe Bend Agroecosystem experiment (n=4), Athens, GA, USA.

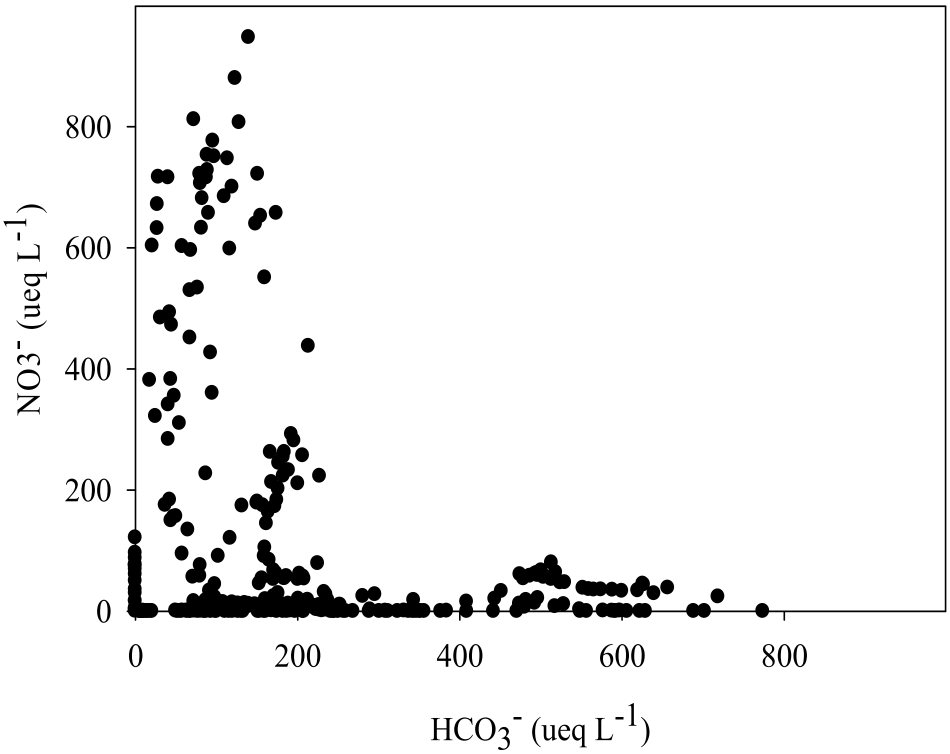


Figure 4.12. Bicarbonate and nitrate concentrations in individual soil water samples at 15 and 100 cm under three land uses (conventional till, no-till, and forest succession) at the Horseshoe Bend Agroecosystem Experiment, Athens, GA, USA, January-July 2008 (n=353). Nine samples with NO_3 concentrations > 1000 μeq L^- are omitted.

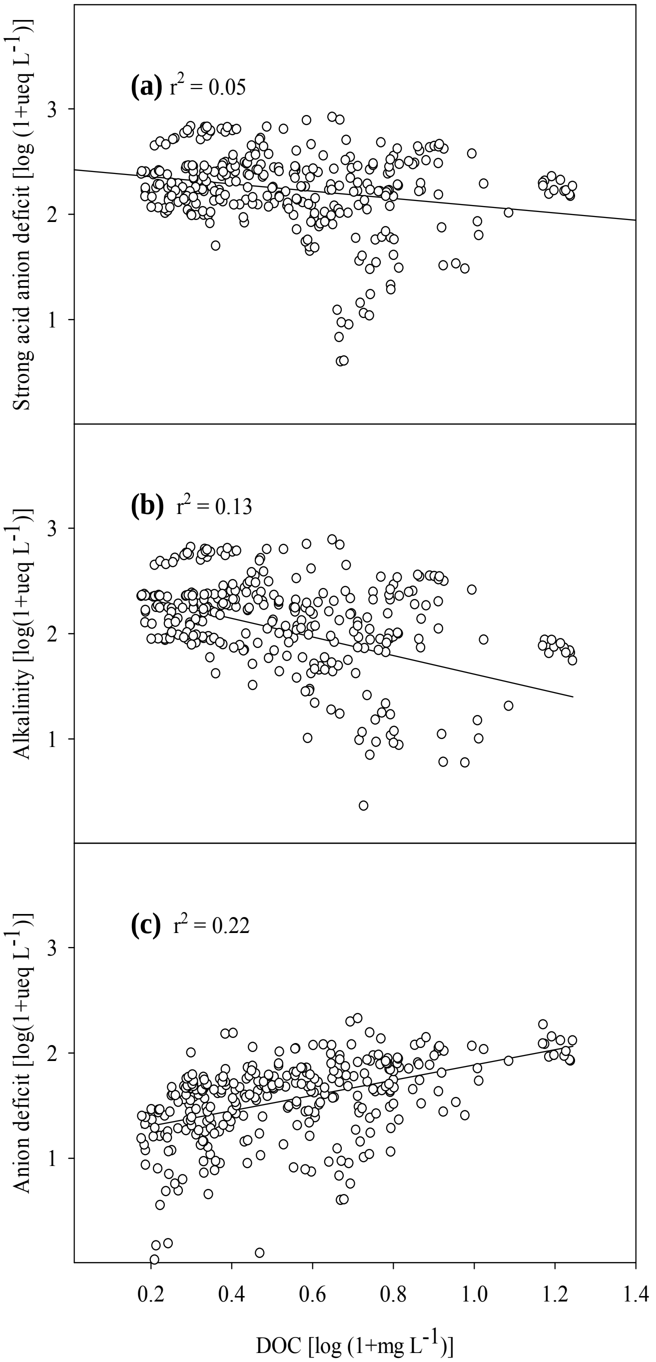
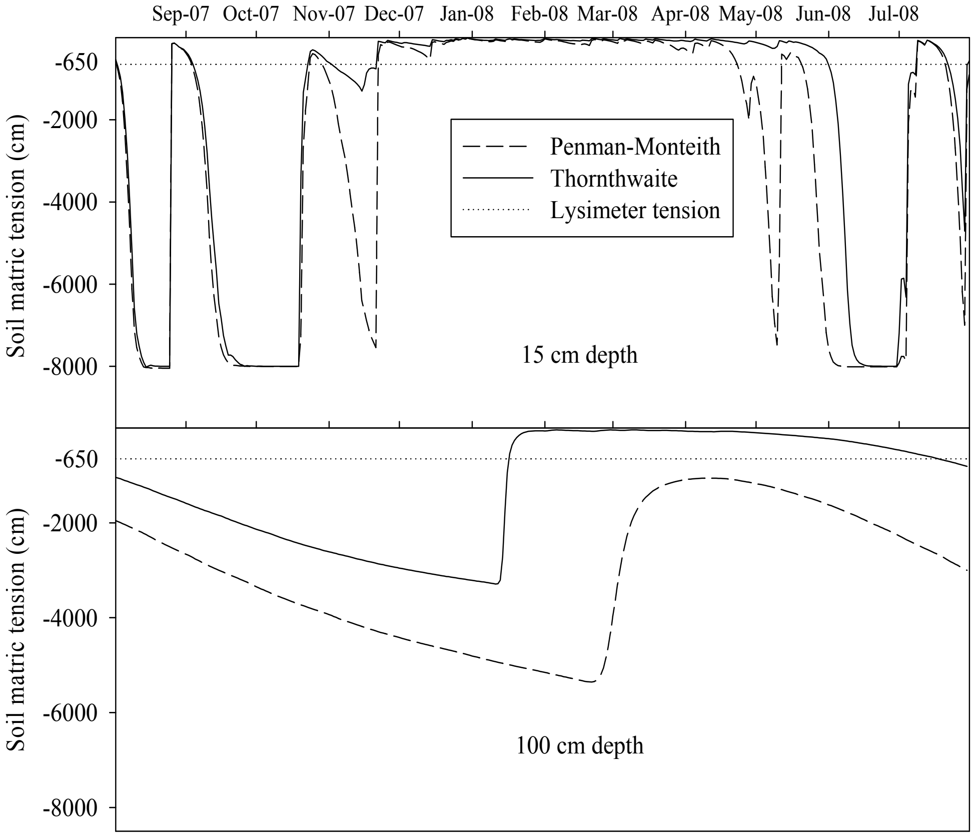


Figure 4.13. Relationships between dissolved organic C (DOC) in lysimeter samples and (a) strong acid anion deficit (b) titratable alkalinity and (c) anion deficit. Anion deficit and strong acid anion deficit are estimated by charge balance including or excluding HCO_3, respectively. Forty-nine samples with negative anion deficit estimates excluded from January-July 2008 samples from Horseshoe Bend, Athens, GA, USA (n=311) under three land use types (conventional till, no-till, or forest succession).



Date	15 cm	100 cm
	------n------	
8/2/07	9	0
8/29/07	11	1
10/25/07	7	0
11/29/07	11	1
12/13/07	9	1
12/18/07	10	2
1/2/08	11	8
1/10/08	11	10
1/18/08	12	8
1/26/08	12	9
2/3/08	12	11
2/10/08	12	11
2/19/08	12	11
3/1/08	12	11
3/9/08	12	11
3/20/08	12	11
3/29/08	12	10
4/4/08	9	9
4/12/08	12	10
4/18/08	12	11
4/25/08	5	10
5/2/08	5	10
5/12/08	6	11
5/21/08	7	8
5/30/08	4	3
6/7/08	0	2
7/8/08	6	1
7/15/08	11	3
7/22/08	7	3

Figure 4.14. Soil matric tensions from HYDRUS model resulting from two potential evapotranspiration calculation methods at 15 cm and 100 cm. When the lysimeter tension line crosses the modeled soil matric tension lines, then a lysimeter collection is theoretically possible. The table on the right shows the number of lysimeters (n) which collected ≥ 10 mL H_2O for a specific date x depth combination. When n=12, then all lysimeters collected H_2O for a particular depth. Comparison of the figure with the table allows for a qualitative validation of the hydrologic models.

Table 4.1. P-values (Tukey's honestly significant difference) for land use contrasts for exchangeable cation concentrations, effective cation exchange capacity (ECEC), and soil pH (0.01M $CaCl_2$) by depth class in the Horseshoe Bend Agroecosystem Experiment, Athens, GA, USA. March 2007 (n=4).

Depth	*Ca*	*Mg*	*K*	*ECEC*	*pH*	*Ca*	*Mg*	*K*	*ECEC*	*pH*	*Ca*	*Mg*	*K*	*ECEC*	*pH*
-cm-	---------------CT-NT----------------					---------------------FS-NT---------------------					-----------------------FS-CT----------------------				
0-5	0.01	0.03	0.96	0.01	0.98	0.03	0.74	0.24	0.12	0.003	0.85	0.10	0.16	0.31	0.007
5-15	0.46	0.45	0.97	0.23	0.33	0.003	0.04	0.03	0.02	<0.0001	0.02	0.23	0.05	0.35	0.0003
15-30	0.88	0.15	0.94	0.47	0.93	0.007	0.005	0.003	0.04	<0.0001	0.01	0.12	0.005	0.24	<0.0001
30-50	0.90	0.02	0.42	0.40	0.91	0.21	<0.0001	0.003	0.02	<0.0001	0.37	0.0003	0.02	0.12	<0.0001
50-100	0.23	0.95	0.84	0.33	0.69	0.003	0.64	0.03	0.005	0.004	0.04	0.81	0.01	0.05	0.001
100-150	0.69	0.79	0.97	0.98	0.72	0.0001	0.42	0.15	0.003	0.05	0.0003	0.79	0.21	0.004	0.01
150-200	0.29	0.92	1.00	0.74	0.96	0.002	0.25	0.86	0.16	0.02	0.02	0.42	0.82	0.43	0.02
0-200	0.12	0.99	1.00	0.26		<0.0001	0.88	0.004	0.0006		0.0003	0.93	0.004	0.005	
0-100	0.30	0.32	1.00	0.11		0.002	0.007	0.006	0.0007		0.02	0.07	0.005	0.02	

CT=conventional till; NT=no-till; FS=42-yr-old Forest Succession

Table 4.2. Exchangeable nutrient contents for 0-2 m soils (means ± 1 SD) at Horseshoe Bend (n=4), Athens, GA, USA, March 2007. Different letters indicate a significant contrast (α=0.1).

Soil Profile	*Ca*	*Mg*[¶]	*K*	*ExAc*	*ECEC*
	------------------------	------------------------	kmol$_c$ ha^{-1}	------------------------	------------------------
Conventional till	555 ± 35^a	78 ± 9^a	27.1 ± 4.0^a	1.2 ± 0.4^a	720 ± 58^a
No-till	621 ± 49^a	87 ± 11^a	26.9 ± 5.4^a	0.7 ± 0.8^a	782 ± 54^a
Forest succession	364 ± 38^b	64 ± 4^b	12.5 ± 4.2^b	42 ± 18^b	565 ± 42^b
(CT+NT)/2 – FS	224 ± 25	19 ± 5	14.5 ± 2.8	-41 ± 6	186 ± 32
Fertilizer input	32.4	24.9	27.0		

[¶] This is the content sum for exchangeable Mg from 0-1 m. From 0-2 m sums were 136 ± 31, 133 ± 39, and 146 ± 42 for CT, NT, and FS, respectively.

Table 4.3. Forest cation contents (mean ± 1 SD) in the soil exchangeable pool (measured in March 2007 from 0-2 m) and forest biomass (measured July 2008) at Horseshoe Bend, Athens, GA, USA. Differences between the forest pool and the average agroecosystem (conventional and no-till) soil exchangeable contents are also shown relative to cumulative fertilizer inputs (1978-2007) to the agroecosystem plots.

Component	*Ca*	*Mg*¶	*K*
	--------------kmol$_c$ ha^{-1}--------------		
Forest soil	364 ± 38	64 ± 4	12.5 ± 4.2
Forest uptake	87 ± 13	12.6 ± 2.6	18.2 ± 2.5
Forest ecosystem	451 ± 37	76.2 ± 3.0	30.6 ± 6.2
(CT+NT)/2 - FE	137 ± 25*	6.5 ± 4.9	-3.6 ± 3.2
Fertilizer inputs	32.4	24.9	27.0

¶ This is the content sum for exchangeable Mg from 0-1 m.

*Asterisk indicates a significant contrast between the forest ecosystem pool and the agroecosystem average soil exchangeable content (CT+NT)/2 (α=0.1).

Table 4.4. Volume-weighted mean (± 1 SD) cation concentrations in solutions under three land use at the Horseshoe Bend Agroecosystem Experiment, Athens, GA, USA. Samples were collected weekly from Nov-2007-Jul-2008. Different letters within a depth and solution component represent a significant difference between land uses (n=4, α=0.1).

Land Use	*Depth*	*Ca*	*Mg*	*K*	*Na*	*NH$_4$*	*H*	*Total cations*
	--cm--	μeq L^{-1}						
Wetfall		14.5	0.7	2.5	6.5	15.6	23.0	62.7
Conventional till	0	123 ± 26^{a}	73 ± 32^{a}	175 ± 35^{a}	9 ± 1^{a}	22 ± 6^{a}	1.2 ± 0.4^{a}	403 ± 79^{a}
No-till		205 ± 19^{b}	219 ± 46^{b}	374 ± 17^{b}	11 ± 1^{b}	47 ± 11^{b}	0.5 ± 0.1^{b}	856 ± 65^{b}
Forest succession		202 ± 36^{b}	105 ± 12^{a}	237 ± 88^{a}	13 ± 1^{c}	21 ± 7^{a}	0.8 ± 0.1^{c}	579 ± 98^{c}
Conventional till	15	612 ± 305^{a}	210 ± 92^{a}	57 ± 20^{a}	28 ± 6^{ab}	1.4 ± 0.3^{a}	0.8 ± 0.3^{a}	908 ± 398^{a}
No-till		471 ± 302^{ab}	155 ± 79^{a}	30 ± 24^{a}	22 ± 4^{b}	0.8 ± 0.5^{b}	1.3 ± 0.6^{a}	679 ± 384^{a}
Forest succession		183 ± 81^{b}	114 ± 57^{a}	55 ± 43^{a}	33 ± 5^{a}	0.6 ± 0.4^{b}	4.4 ± 5.0^{a}	389 ± 135^{a}
Conventional till	100	535 ± 138^{a}	121 ± 51^{a}	22 ± 10^{a}	27 ± 7^{a}	0.6 ± 0.5^{a}	0.9 ± 0.2^{a}	706 ± 192^{a}
No-till		533 ± 246^{ab}	113 ± 58^{ab}	7 ± 4^{b}	21 ± 4^{a}	0.5 ± 0.2^{a}	0.8 ± 0.2^{a}	676 ± 304^{ab}
Forest succession		260 ± 68^{b}	44 ± 11^{b}	6 ± 5^{b}	41 ± 9^{b}	1.5 ± 1.1^{a}	1.2 ± 0.2^{a}	354 ± 72^{b}

Table 4.5. Contribution of titratable alkalinity (HCO_3) and the anion deficit to charge balance (means ± 1 SD, n=3 or 4). Estimate based upon seven-month volume-weighted means by plot at Horseshoe Bend, Athens, GA, USA, Jan-Jul 2008. Different letters within a depth and solution component represent a significant difference between land uses (n=4, α=0.1).

Land use	*Depth*	*Alkalinity*	*Total inorganic anions†*	*Anion deficit¶*
	--cm--	-------------------------ueq L^{-1}	------------------------	
Wetfall		0	52.9	9.9
Conventional till	0	$109 \pm 41^{\ddagger a}$	249 ± 64^{a}	22 ± 7^{a}
No-till		$390 \pm 90^{\ddagger b}$	631 ± 114^{b}	63 ± 16^{a}
Forest succession		$253 \pm 71^{\ddagger c}$	414 ± 77^{c}	166 ± 47^{b}
Conventional till	15	261 ± 201^{a}	878 ± 448^{a}	36 ± 32^{a}
No-till		130 ± 121^{a}	610 ± 371^{a}	47 ± 10^{a}
Forest succession		92 ± 133^{a}	326 ± 105^{a}	58 ± 27^{a}
Conventional till	100	241 ± 184^{a}	686 ± 202^{a}	16 ± 9^{a}
No-till		294 ± 235^{a}	644 ± 307^{ab}	25 ± 10^{ab}
Forest succession		119 ± 40^{a}	316 ± 61^{b}	37 ± 16^{b}

¶ Anion deficit (Organic anion estimate) = Total cations –Total inorganic anions

† Sum of Cl, NO_3, SO_4, PO_4, and HCO_3

‡ Alkalinity not necessarily HCO_3^-. See discussion in text.

Table 4.6. Volume-weighted mean (± 1 SD) anion concentrations in solution by land use from weekly collections at Horseshoe Bend, Athens, GA, USA, Nov-2007-Jul-2008. Different letters within a depth and solution component represent a significant difference between land uses (n=4, α=0.1).

Land use	*Depth*	*Cl*	*NO_3*	*PO_4*	*SO_4*	*Strong acid anion deficit*¶
	--cm--	---------------------------------	---------------------------------	μeq L^{-1}	---------------------------------	---------------------------------
Wetfall		8.2	13.7	*	30.9	
CT	0	60 ± 8^{a}	21 ± 3^{a}	33 ± 11^{a}	52 ± 4^{a}	237 ± 69^{a}
NT		46 ± 5^{b}	53 ± 29^{a}	111 ± 29^{b}	64 ± 3^{b}	583 ± 44^{b}
FS		32 ± 8^{c}	33 ± 20^{a}	25 ± 7^{a}	64 ± 7^{b}	423 ± 91^{c}
CT	15	46 ± 24^{a}	385 ± 427^{a}	*	193 ± 59^{a}	283 ± 184^{a}
NT		21 ± 3^{a}	373 ± 439^{a}	*	113 ± 36^{a}	172 ± 113^{a}
FS		55 ± 29^{a}	16 ± 28^{a}	*	172 ± 70^{a}	147 ± 145^{a}
CT	100	29 ± 4^{a}	248 ± 303^{a}	*	171 ± 47^{a}	258 ± 186^{a}
NT		37 ± 4^{a}	205 ± 314^{a}	*	114 ± 96^{a}	320 ± 226^{a}
FS		71 ± 19^{b}	5 ± 5^{a}	*	121 ± 61^{a}	157 ± 55^{a}

¶ Strong acid anion deficit = total cations –strong acid anions (sum of Cl, NO_3, PO_4, and SO_4)

* <1 ueq L^{-}

Table 4.7. Long-term averages and short-term estimates from HYDRUS model using two potential evapotranspiration calculation methods. Values in parentheses show flux estimates from the long-term model in which monthly precipitation is distributed evenly among time-steps, Horseshoe Bend, Athens, GA, USA.

	1978-2007		*August 2007- July 2008*	
	Thornthwaite	Penman-Monteith	Thornthwaite	Penman-Monteith
	---------------------------cm H_2O yr^{-1}--------------------------			
PET	88.7	122.5	95.4	141.6
Precipitation	-------117--------		-------89.4------	
0 cm	-------87.3-------		-------67.1------	
15 cm	58.4	48.3	42 (38)	31.4 (26)
100 cm	23.8	7.6	13.7 (12.4)	0.007 (0)

Table 4.8. Comparison of annual leaching rates under different land uses through time in relation to annual forest uptake. Nutrient leaching rates for 1978-1980 are from Stinner et al. (1984) at 60 cm depth. Leaching rates for 2007-2008 at 15 and 100 cm depth are measured concentrations and simulated water fluxes. Simulated water fluxes are shown from 1978-1980 for comparison. Horseshoe Bend, Athens, GA, USA.

Land use	*Period*	*depth*	*HYDRUS flux*	*Ca*	*Mg*	*K*
		------cm-------		--kmol$_c$ ha^{-1} yr^{-1}--		
Conventional till	Jun-78-May-79	60	26.0	1.40	0.41	0.05
No-till				0.85	0.49	0.08
Conventional till	Jun-79-May-80	60	27.2	3.19	1.23	0.15
No-till				2.59	1.32	0.23
Forest succession				1.50	0.58	0.03
Conventional till	Aug-07-Jul-08	15	42.0	2.57	0.88	0.24
No-till				1.98	0.65	0.12
Forest succession				0.77	0.48	0.23
Conventional till	Aug-07-Jul-08	100	13.7	0.73	0.17	0.03
No-till				0.73	0.15	0.01
Forest succession				0.36	0.06	0.01
Annual forest uptake	1966-2008	NA	NA	2.07	0.30	0.43

Table 4.9. Reworking of Table 3 from Stinner et al. (1984) for the purpose of charge balance. Concentrations based upon solutions collected from Jul-Nov-1979.

Land Use	*Depth*	*Ca*	*Mg*	*K*	*NH_4*	*Total cations*	*NO_3*	*Total cations – NO_3*
		μeq L^{-1}						
Conventional till	60 cm	1542	355	91	8	1996	562	1434
No-till		953	274	98	31	1356	327	1029
Forest Succession		439	120	52	36	647	100	547

CHAPTER V

SOIL AGGREGATE DISTRIBUTIONS AND ASSOICATED ORGANIC MATTER AFTER THREE DECADES UNDER CONVENTIONAL TILLAGE, NO-TILL, AND FOREST SUCCESSION[3]

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[3] S. Devine, D. Markewitz, and P.F. Hendrix. To be submitted to: *Soil Science Society of America Journal*

Abstract

The effect of converting farming practices from conventional till (CT) to no-till (NT) on soil organic C (SOC) storage is of interest. Previous work at Horseshoe Bend (HSB), a 30 year experiment comparing NT and CT, found that NT enhanced aggregate stability and increased SOC contents to 5 cm. Our objectives were to compare soil structure and SOC fractions to depths previously not studied at HSB, to include adjacent land undergoing forest succession (FS) to the study, and to establish a soil moving experiment (SME) to monitor short-term changes in SOC and soil structure. Soils were sampled to 28 cm and structural stability was estimated by comparing mean-weight diameters obtained from dry and wet sieving soils. Total SOC, particulate organic C (POC, 53-2000 μm), and fine C (< 53 μm) were measured in water-stable aggregate fractions. Total SOC, structural stability, and microbial biomass C (MBC) were also determined for the SME soil to 15 cm one year after its installation. Enhanced stability under NT compared to CT was limited to a depth of 5 cm, while enhanced stability under FS compared to CT occurred to a depth of 28 cm and compared to NT from 5-28 cm. Increases in SOC concentrations generally followed the increases in stability, except that no differences in SOC fractions were observed from 15-28 cm, suggesting that greater stability does not necessarily imply greater SOC storage. Approximately half of the differences in SOC were due to differences in POC, highlighting its importance in SOC models. An increase in SOC was observed in the SME soil under FS, which could be explained by mixing with 10-20% of the native FS soil. Enhanced structural stability of the SME soil under FS was not linked to significant increases in MBC and could not be explained by mixing with native FS soil. The importance of macroaggregate stability was also observed from 5-15 cm in the SME where a reduction from the initial 0.92 to 0.82-0.84 g C kg^{-1} soil occurred under all three land uses.

Introduction

Understanding the mechanisms for soil carbon storage and stabilization is becoming increasingly relevant as human activity is recognized as a major factor in climate change and as soil organic carbon (SOC) is known to be a major pool of global C. Since physical protection of SOC within stable soil aggregates is considered to be one of the major SOC stabilization mechanisms, (Mikutta et al., 2006; Six et al., 2002a; von Lutzow et al., 2006), the effects of land management on aggregate stability are accepted as key factors in determining SOC levels (Six et al., 1998). Although criticism of soil aggregate-focused research has argued that researchers are giving too little attention to the regulatory role of soil porosity (Young et al., 2001), there is substantial evidence that aggregates have boundaries with ecological significance, elucidated with a variety of methods under a range of conditions (Golchin et al., 1994; Hassink et al., 1993; Jasinska et al., 2006; Rasmussen et al., 2005; Vreeken-Buijs et al., 1998).

Structural protection mechanisms are generally envisioned to operate through pore size exclusion of extracellular enzymes, microbes, and soil micro-fauna, in addition to pore-mediated regulation of the environmental factors that control microbial activity, such as oxygen concentration, temperature, and water content. The key concept is that intra-aggregate pores are finer (and perhaps more tortuous) than inter-aggregate pores, that is, the larger pores surrounding aggregates (Horn et al., 1994), so that decomposition is slowed within aggregates. The abundant research on the relationship between soil aggregation and SOC stabilization has produced several contrasting models of how physical protection of SOC occurs.

The classic aggregate hierarchy model suggests that soil structure arises from aggregation of fine mineral particles into microaggregates (53 μm to 250 μm) continuing to aggregate to macroaggregates (>250 μm) with increasing dependence on greater and more transient organic binding agents as the scale increases (Tisdall and Oades, 1982). In soils demonstrating aggregate hierarchy, SOC concentration should increase with the increasing aggregate size, since macroaggregates are composed of microaggregates and microaggregate associated SOC plus the SOC binding these microaggregates together into water-stable macroaggregates. Subsequent studies attributed the loss of SOC in cultivated soils to exposure of the SOC responsible for binding microaggregates into macroaggregates to microbial attack (Elliott, 1986).

Oades (1984) modified the aggregate hierarchy theory and hypothesized that microaggregates formed around particulate organic C (POC, 53-2000 μm) enmeshed within macroaggregates. Following this hypothesis, recent work in no-till and afforested systems suggests that decreased macroaggregate turnover in soils lacking mechanical disturbance results in higher SOC due to higher rates of microaggregate formation and stabilization of fine POC (53-250 μm) (Six et al., 2000a; Six et al., 2002b), not an increase in the organic binding agents that hold macroaggregates together. Following this line of thinking, loss of SOC in cultivated soils is explained by shorter macroaggregate turnover times and a reduced opportunity for formation of microaggregates around a fine POC core. POC not occluded within aggregates is referred to as an unprotected, labile pool (Six et al. 2002b). In a review of POC and the conceptually similar light fraction, these labile fractions have been referred to broadly as the "physically uncomplexed" pool of SOC (Gregorich et al., 2006). More recently, it has been hypothesized that increased pore connectivity in soils that are not tilled allows greater movement of dissolved organic carbon (DOC) from larger pores surrounding aggregates into intra-aggregate pore spaces, a flux which may be enhanced by wetting-drying cycles (Smucker et al., 2007). In tilled soils, disruption of the pore network effectively isolates substantial portions of the intra-aggregate pore space from replenishment of DOC by root exudates, decomposition of

POC, or litter leachate laden with DOC. Smucker et al. (2007) argue that proper management has the potential to “double or triple soil carbon levels” if these mechanisms are fully understood. The focus on DOC by Smucker et al. (2007) is in opposition to other work that has identified POC as the fraction of SOC most susceptible to management and soil structural disruption (Cambardella and Elliott, 1992; Causarano et al., 2008; Chan, 2001; Franzluebbers and Arshad, 1997; Skjemstad et al., 2006; Tiessen and Stewart, 1983; Wander et al., 1994). Size fractionation of SOC offers a relatively simple way to address the difference in the proposed mechanisms put forth by Six et al. (2002b) and Smucker et al. (2007). If micro-scale fluxes of DOC are important to attaining maximum SOC storage capacity, then this should be recovered as fine C (<53 μm) in systems where significantly higher levels of SOC have been attained.

The overall research objective of this study was to expand upon the use of SOC and soil aggregate fractionation techniques used previously at the 30 year old agroecosystem experiment at Horseshoe Bend (HSB), Athens, GA, USA, and to interpret the results in terms of the aforementioned models of SOC stabilization (Arce Flores and Coleman, 2006; Beare et al., 1994a). This work attempts to describe the effects of three-decades of continuous conventional tillage agriculture, no-till agriculture, and forest succession to depths previously not studied at HSB on (i) both dry and water-stable aggregate size fractions, (ii) a single structural stability indicator derived from aggregate size distribution metrics, and (iii) SOC concentration and composition within aggregate size fractions. In addition a soil moving experiment was carried out to determine the extent to which destructured soil can re-develop macroaggregate stability in the field and, if so, whether or not differences in stability are linked to differential recovery of soil microbial biomass. Also, by destroying large (> 1 mm) soil macroaggregates, I sought to examine the effects of macroaggregate protection on SOC under field conditions as opposed to under laboratory incubations (Beare et al., 1994b; Bossuyt et al., 2002).

Methods

Site Description

The Horseshoe Bend (HSB) agroecosystem experiment (33° 57’ N, 83° 23’W) in Athens, GA, USA, is a long-term comparison of conventional and no-tillage treatments begun in 1978. Based on a series of aerial photos, HSB had been cleared entirely of trees except for a narrow strip along the Oconee River at least since 1938 (Figure 3.2). The site was mostly used for pasture and forage production until 1965 when the Institute of Ecology acquired HSB for research (Hendrix, 1997). The area underwent secondary succession in 1966 except for the future agroecosystem site, which was tilled to plant a crop of millet for a separate, earlier study (Barrett, 1968). Afterwards, the site went fallow and was used for a prescribed burn study and a N fertilization study (Bakelaar and Odum, 1978; Odum et al., 1973). In 1978, the study area was divided into equal numbers of conventional and no-till 0.1 ha plots, and the old-field vegetation was mowed (Hendrix, 1997). Since the experimental plots were in fallow from 1966, the current no-till plots have not been tilled for forty-two years. Conventional tillage has been performed twice annually in most years with moldboard plowing to a depth of 15 cm, followed by disking. In 1981, each agricultural plot was split into different winter crop treatments with winter rye (*Secale cereale* L.) grown on half of each plot and N-fixing crimson clover (*Trifolium incarnatum* L.) grown on the other half until 1984 and then again from 1989 to the present (Coleman et al., in press; Hendrix, 1997). In my soil sampling efforts, I sought to estimate an average effect of no-tillage and conventional tillage on the measured properties by sampling equally between clover and rye split-plots before compositing.

Three secondary, hardwood forest plots adjacent to the tillage experiment and a fourth afforested plot approximately 80 m to the west of the experiment were established in 2007 (Figure 3.2). These areas were intended to represent a third treatment, referred to herein as forest succession. All plots were on the same terrace as the agroecosystem plots and were observed to be part of the same cleared area in the aerial photograph (Figure 3.2). Most likely, these afforested plots were not tilled in 1966, which means they essentially underwent a pasture to forest conversion. The soils under all three land uses have been re-classified from a clayey, kaolinitic, thermic, Rhodic Kanhapludult (Beare et al., 1997) to a fine-loamy, kaolinitic, thermic, Typic Kanhapludalf based on new particle-size analysis data in the control section and measurements of base saturation that are >98% in all three treatments at 140 cm (i.e., 125 cm below the top of the kandic horizon).

Aggregate size fractions and stability

In order to quantify aggregate stability, separate samples were obtained at the end of the summer growing season in October 2007 using a 5 cm diameter corer attached to a slide-hammer to a depth of 28 cm. Each core was divided into 0-5, 5-15, and 15-28 cm and passed through a 10 mm mesh by gently breaking the cores along planes of weakness before air-drying. These samples were dry-sieved through 6.3, 4, 2, and 1 mm screens to obtain dry aggregate size classes. A separate subsample of the < 1 mm dry aggregates was sieved on a 0.25 mm screen. The objective of dry-sieving was not to estimate dry aggregate stability (Nimmo, 2002) but to determine the initial aggregate size distribution before wet-sieving. Sub-samples of 50 g were then weighed out by re-combining all the dry aggregate size classes according to their proportional mass for a whole sample. This ensured that each sub-sample accurately represented the whole-soil dry aggregate size distribution for a whole sample. This has been acknowledged as a methodological issue in determining aggregate size distributions (Kemper and Chepil, 1965). These 50 g sub-samples were then wet-sieved with a modified Yoder (1936) apparatus that is made to process larger masses of soil on nested sieves (21.6 cm) and to permit complete recovery of all soil from each sample. The method obtains four aggregate size classes: (i) > 2 mm; (ii) 0.25 - 2 mm; (iii) 0.053-0.25 mm; and (iv) <0.053 mm. Wet aggregate mean-weight diameters (MWD) were calculated by multiplying the proportion of soil in each of these four aggregate size classes by the mid-point of the size class. The calculation of the dry MWD used the same size divisions as the Wet MWD except no <0.053 mm fraction was included, since dry sieving material through a 0.053 mm sieve is not practical. The aggregate stability index was then calculated by dividing the Wet MWD by the Dry MWD; an index of 1 represents perfect structural stability.

Soil organic C fractionation and determination

Soil sub-samples were pulverized in a Spex 8200 ball-mill grinder and total soil organic C (SOC) and N was determined using dry combustion on a CE Elantech NC 1110 analyzer (Lakewood, NJ). To obtain particulate organic carbon (POC) and fine-C fractions, a 3-5 g subsample of each aggregate size fraction was dispersed by adding 15-25 mL of 0.5% Na-hexametaphosphate and shaking in 50 mL centrifuge tubes for 16 h on a reciprocal shaker at 200 rpm. The resulting soil slurry was washed through a 53 µm sieve using 0.5 L of DI water to fractionate the soil into: (1) sand + POC and (2) silt + clay + fine-C. A rubber policeman was used to aid in dispersion of stable soil aggregates on top of the 53 μm sieve when necessary. Fine-C and POC fractions were also pulverized and C and N determined. A mass correction was made for the amount of Na-HMP recovered in the fine fraction prior to estimation of fine-C and N concentrations.

Since the <53 μm fraction does not contain sand, total SOC and POC are calculated on a sand-free basis for each aggregate size fraction in order to make comparisons among all the aggregate size classes (Elliott et al., 1991):

g POC kg^{-1} sandfree aggregate = (g POM-C kg^{-1} sand)*(kg sand kg^{-1} silt + clay)

g SOC C kg^{-1} sandfree aggregate = (g SOC kg^{-1} soil)*(kg soil kg^{-1} silt + clay)

Soil moving experiment

A soil moving experiment (SME) was carried out to determine the extent to which destructured soil re-develops aggregate stability among the different land uses. First, CT soil was collected from all four plots, dried at 60° C in a forced-air oven, and crushed with a rolling pin to destroy larger macroaggregates and to pass a 1 mm sieve, referred to henceforth as “initial soil.” A 10 cm diameter auger was used to remove soil to 20 cm depth from four locations in each CT, NT, and FS plot at the end of July 2007. A PVC pipe of an equal diameter was placed as an insert in each hole to prevent the side walls from collapsing during filling. Each SME hole was then filled with the initial soil and uniformly tamped with a capped PVC pipe to a bulk density of approximately 1.4 g soil cm^{-3}. Soil packing was tested with success in the laboratory by filling the same PVC pipe insert to the desired bulk density. The insert was removed after packing, and the edge of the SME core marked with flags and aluminum nails. At the end of August 2008, the same 5 cm diameter corer previously used to sample aggregates was used to extract a smaller soil core within the 10 cm diameter SME core. All cores were located (some with the aid of a metal detector), divided into 0-5 and 5-15 cm depth classes, and composited by land use. In one FS plot, only two cores were sampled due to obvious mixing with native soil that had occurred from animal activity; in three other plots (two CT and one FS), only three cores were sampled for the same reason.

The same procedure as described above was used to measure aggregate stability and total SOC and N in the two depth classes. Microbial biomass C and N was also determined on field moist, replicate subsamples following the 24 hour chloroform fumigation—K_2SO_4 extraction procedure (Vance et al., 1987). Extracts were analyzed for total nitrogen (TN) and non-purgable organic carbon (NPOC) after acidification to pH 2 and sparging with CO_2-free air for 3 minutes (Shimadzu TOC 5000, Columbia, Maryland, USA). Microbial biomass C (MBC) and microbial biomass N (MBN) were estimated using the following equations (Brookes et al., 1985; Wu et al., 1990):

$$\text{MBC} = (\text{NPOC}_{\text{fumigated}} - \text{NPOC}_{\text{non-fumigated}})*2.22$$

$$\text{MBN} = (\text{TN}_{\text{fumigated}} - \text{TN}_{\text{non-fumigated}})*1.87$$

Results

Aggregate size distributions and stability

Aggregate stability, as defined by the wet-sieved mean weight diameter (MWD) divided by the dry-sieved MWD, decreased significantly from FS (0.98±0.01 and NT (0.96±0.04 to CT (0.73±0.10 in the upper 5 cm (Devine, 2009, Table 3.4). In the 5-28 cm layer FS soil was significantly more stable than both NT and CT (Devine, 2009, Table 3.4). This response can also be seen as: (i) a larger percentage of wet-sieved, large macroaggregates (>2000 μm) found in the FS and NT soils from 0-5 cm compared to CT and more large macroaggregates in FS from 15-28 cm compared to both CT and NT and (ii) a higher proportion of the finest (<53 μm) contents under CT compared to both NT and FS from 0-15 cm (Figure 5.1). In the 0-5 cm depth class, there was very little change in the size distribution from dry-sieved to wet-sieved aggregates for both NT and FS soils (Devine, 2009, Table 3.4). .

Aggregate associated total, fine, and particulate organic carbon (POC)

Among land uses, there were consistent differences in C concentrations within wet-sieved aggregate size classes. From 0-5 cm, NT and FS aggregate size fractions were significantly elevated for all C fractions compared to CT with one exception: the large macroaggregates under NT were significantly lower in all C fractions compared to the FS soil and not significantly different with respect to total and POC compared to CT (Figure 5.2). From 5-15 cm, there were no significant differences between CT and NT for any of the size class and C fraction combinations, while FS aggregate size classes >53 μm were significantly elevated with respect to total and POC (Figure 5.3). There were no significant differences for any of the size class and C fraction combinations from 15-28 cm (Figure 5.4).

Overall, the majority of C at HSB under all land uses is contained in the water-stable macroaggregate fraction to a depth of at least 28 cm (Figure 5.5). By summing the C contribution from each aggregate size fraction to calculate a C concentration for each depth class by treatment combination, differences in POC explained 34% of the total SOC difference between NT and CT, 43% of the total SOC difference between FS and CT, and 51% of the total SOC difference between FS and NT. From 5-15 cm, differences in POC explained 56% of the difference between FS and CT and 47% of the difference between FS and NT.

In terms of significant differences among the aggregate size classes within a land use and depth class, the most consistent result was that the <53 μm aggregate fraction had lower total SOC concentrations when expressed on a sand-free basis (Figures 5.2-5.4). From 0-15 cm, there were no significant differences among the size classes >53 μm under FS (Figures 5.2 and 5.3). There were also no significant differences in POC among the aggregate size classes for any of the depth classes under FS (Figures 5.2-5.4).

In the upper 15 cm of the NT soils, both the large macroaggregates and the <53 μm fractions were carbon depleted relative to the small macroaggregates (250-2000 μm) and microaggregates (Figures 5.2 and 5.3). Under CT from 0-5 cm, the small macroaggregates (250-2000 μm) were significantly elevated in total and POC compared to the other size fractions (Figure 5.2). From 5-15 cm, both the small macroaggregates and microaggregates were significantly elevated in total SOC compared to the large macroaggregates, while only the small macroaggregates were significantly elevated in POC compared to the large macroaggregates (Figure 5.3). From 15-28 cm, the large macroaggregates were the most carbon rich under all land uses, having significantly greater total SOC and fine C concentrations compared to the <250 μm size fractions (Figure 5.4).

Structural recovery (soil moving experiment (SME))

The SME soil under FS showed significantly greater aggregate stability compared to both CT and NT at 0-5 and 5-15 cm after one year (Table 5.1). There were no significant differences in aggregate stability between CT and NT at either depth in the SME (Table 5.1). Overall, aggregate stability was significantly greater from 0-5 cm compared to 5-15 cm under NT and FS. This depth stratification did not occur under CT (Table 5.1).

C and N losses and gains during the SME

While total N in the SME soil was elevated in FS compared to CT and NT, the difference was not significant ($p>0.2$) (Table 5.2). Total SOC, however, was significantly elevated in the FS soil compared to CT ($p=0.08$) and compared to NT ($p=0.03$) (Table 5.2). The differences could, however, be explained by mixing of 9-20% of unprocessed forest soil with the SME soil for all four afforested plots (Table 5.3). From 5-15 cm, all three land uses had lower concentrations of C and N after one year compared to the initial concentrations, ranging from 8.25-8.41 g C kg^{-1} soil from the initial 9.24 and from 0.71-0.73 g N kg^{-1} soil from the initial 0.81 (Table 5.2).

Changes in microbial biomass during the SME

SME microbial biomass carbon (MBC), like aggregate stability and total SOC from 0-5 cm, was elevated in FS relative to the agroecosystem, though not significantly ($p>0.27$) (Figure 5.6). Overall, there were no significant differences among the land uses from 0-5 cm in terms of MBC and MBN concentrations. Both CT and FS MBC were significantly elevated compared to NT from 5-15 cm ($p=0.02$ and 0.10, respectively) with no differences in MBN at this depth (Figure 5.6). For all three land uses, there was a significant depth stratification in microbial biomass, with MBC and MBN higher and the MBC:N ratio lower from 0-5 compared to 5-15 cm (Figure 5.6).

Discussion

Changes in soil structure and SOC after 30 years of different management

The increase in structural stability under NT compared to CT was limited to a depth of 5 cm, while the FS soil demonstrated significantly greater stability compared to CT to a depth of 28 cm and compared to NT from 5-28 cm (Devine, 2009, Table 3.4). Similarly, previous work at Horseshoe Bend (HSB) on individual aggregate size fractions showed that all aggregates >106 μm from 0-5 cm were significantly more stable in NT compared to CT using a turbidimetric approach to quantifying stability; from 5-15 cm, only the large macroaggregates (>2000 μm) were more stable in NT (Beare et al., 1994a). The difference in aggregate stability between NT and FS from 5-15 cm is not evident from examination of the wet-sieved aggregate size classes (Figure 5.1), since the initial dry aggregate size distributions differed slightly (Devine, 2009, Table 3.4). The aggregate stability metric showed lower coefficients of variation within a land-use than did either the dry or wet mean-weight diameter within a land use and so may be more sensitive to the effects of land use on soil structure than analysis of aggregate size distributions produced from one methodology . Other researchers have recommended using multiple methodologies in characterizing aggregate size distributions in order to draw robust conclusions about the effects of land management (Beare and Bruce, 1993).

Significant differences in SOC were evident among the land uses in different aggregate size fractions. Both NT and FS generally had elevated concentrations in all fractions compared to CT from 0-5 cm with increases in POC explaining 40-50% of concentration differences (Figure 5.2). This lends support to the conceptual models of both Six et al. (2000a), who emphasize stabilization of POC within microaggregates formed in stable macroaggregates, and Smucker et al. (2007), who emphasize the maintenance of pore connectivity to usher DOC into unsaturated micropores (with respect to C), since both POC and fine C contributed equally to concentration differences in aggregate size fractions. The effect of tillage could be seen in two different ways: (1) a direct disruption of the pore-network, creating isolated portions of the soil matrix and/or (2) the destruction of soil aggregates by mechanical action and by exposure to the direct, pounding effects of rainfall, which expose SOC to the action of microbes.

The FS soil had elevated concentrations of SOC from 5-15 cm compared to NT for macro- and microaggregates and compared to CT for microaggregates with the increases in POC explaining 35-60% of the concentration differences (Figure 5.3). Previous work has also shown no differences in SOC concentrations among the aggregate size fractions from 5-15 cm for CT and NT at HSB (Arce Flores and Coleman, 2006; Beare et al., 1994a; Beare et al., 1997; Bossuyt et al., 2002), but this is the first time that aggregation has been studied below 15 cm. While differences in aggregate stability were evident below 15 cm, significant differences in SOC fractions among the aggregate size fractions were not evident (Figure 5.4). This suggests that the increased aggregate stability is not necessarily linked to increased stabilization and storage of SOC.

Although, at present, there is much interest in aggregates and SOC storage, aggregate research developed from interest in soil erosion (Yoder, 1936). Although water-stability may be an indirect measure of SOC protection (Beare et al., 1994b), wet sieving for aggregates is more a test of soil's tensile strength than any direct measure of the soil's capacity to physically protect SOC from decomposition. Aggregate size distributions are, in fact, a direct function of the amount of energy used to disrupt the soil structure. Theorizing about SOM dynamics from aggregate size distribution results should therefore be done cautiously.

Nonetheless, comparing the different aggregate size fractions within a land use may offer some additional clues about SOC cycling. Within the FS soil from 0-15 cm, only the wet-sieved fine fraction (<53 μm) had a significantly lower C concentration within each depth class (Figures 5.2 and 5.3), demonstrating the importance of coarser SOC to total SOC. The similar concentrations among the FS macro- and microaggregates suggest that an equilibrium exists with respect to their turnover with no evidence of aggregate hierarchy. Similar proportions of POC are also found in FS macroaggregates and microggregates, suggesting that mechanisms of decomposition are similar, regardless of the size of the aggregate (Table 5.4).

In the agroecosystem soils, large macroaggregates (>2000 μm) and the fine fraction were generally depleted in total SOC compared to the small macroaggregates (250-2000 μm) and microaggregates (53-250 μm). This result is inconsistent with hierarchy theory. Large macroaggregates under CT have significantly lower proportions of POC compared to small macroaggregates at all depths (Table 5.4) and under NT large macroaggregates had significantly lower proportions of POC compared to small macroaggregates and microaggregates (Table 5.4).

In previous research at HSB, Beare et al. (1994a) observed the highest C concentrations in the large NT microaggregates (106-250 μm) compared to the macroaggregates from 0-5 cm and speculated that this was due to formation of microaggregates around decomposing residues in stable macroaggregates, followed by their release upon macroaggregate breakdown, as originally formulated by Oades (1984). Work that followed this at HSB also found the highest C concentrations in the microaggregate class from 0-5 cm in NT (Bossuyt et al., 2002) but this result was not found in more recent (Arce Flores and Coleman, 2006) or the present work (Figure 5.2).

An alternative explanation for the decrease in carbon concentration in large macroaggregates would be that they have become relatively isolated from biological activity and have developed lower rates of incorporation of new carbon with old carbon gradually decomposed through the years. Fire ants have invaded the agroecosystem field but are not present in the forest and could be affecting agroecosystem earthworm populations and incorporation of POC into large macroaggregates. Also, lower rates of incorporation may simply be due to lower residue inputs in the agroecosystem in recent years from low cotton yields (Coleman et al., in press). Previous research also supports the hypothesis that the center of large macroaggregates can become isolated from incorporation of new C. A ^{14}C tracer study at HSB found that macroaggregates had ^{14}C concentrations that were half that of ^{14}C concentrations in microaggregates after 3 years of addition of labeled crop litter (Bossuyt et al., 2002). While it is possible that the carbon had cycled through macroaggregates with residual ^{14}C ultimately becoming stabilized in microaggregates, this seems unlikely. In more recent ^{13}C work at HSB, it was observed that the large NT macroaggregates (18%) had the lowest rates of incorporation of new carbon compared to the small NT macroaggregates (31%) and NT microaggregates (23%) after two full growing seasons of a conversion from mixed C_4/C_3 crops to only C_3 crops. However, within 7 years large macroaggregates, small macroaggregates, and microaggregates all had 38-41% new carbon (Arce Flores and Coleman, 2006).

Finally, aggregate hierarchy, which suggests that intermicroaggregate organic matter should increase C concentration of stable macroaggregates compared to microaggregates, is only evident in the 15-28 cm depth class (Figures 5.2-5.4). Total SOC clearly decreases from the large macroaggregates through the smallest fraction (<53 μm) in the 15-28 cm depth class under all land uses. The method for isolating water-stable aggregates used repeatedly at HSB may not be forceful enough to isolate large macro-aggregates of higher C concentration in the upper 15 cm. If a more forceful fractionation procedure was used, such as sonication, then perhaps low C macroaggregates would be dispersed and their particles transferred to smaller fractions. Previous research has also shown that wet-sieving of pre-wetted soil does not support aggregate hierarchy theory, as was done in this study, while slaking dry soil does (Elliott, 1986). Also, aggregate hierarchy has been shown to be less apparent in soils dominated by 1:1 clays with high oxide contents like at HSB compared to soils dominated by 2:1 clays with low oxide contents (Oades and Waters, 1991; Six et al., 2000b).

Soil moving experiment

In order to study the rate at which soil stability recovers among different land uses, an experiment was designed to compare re-aggregation, recovery of microbial C, and changes in total SOC within destructured soil. Significant differences in aggregate stability were evident after moving crushed and sieved (1 mm) soil from the CT plots back to each land use for both the 0-5 and 5-15 cm depth classes after one year (Table 5.1), suggesting that water-stable macroaggregates can be formed rapidly under the different land uses but most quickly under forest succession. Similar rapid changes in soil structure were observed in a soil moving experiment in the tropics where larger blocks of soil were transferred from forest to pasture and vice-versa to study the effects on an invasive earthworm species (Barros et al., 2001).

Possible native forest soil mixing with the SME soil cannot explain the observed increase in water-stable aggregates (Table 5.3). Anecdotal evidence also suggests that the increase in water-stable aggregates under FS was not simply due to SME soil mixing with native soil. While capillary pre-wetting of 0-5 cm indigenous FS soil was notoriously difficult due to hydrophobic properties, the SME soil from FS became immediately moist from capillary rise after placing the soil on top of the sieve. Previous work in the HSB agroecosystem demonstrated the importance of fungal hyphae in stabilizing aggregates by treating subplots with fungicides followed by measurement of aggregate size distributions (Beare et al., 1997). Since forest soils are thought to be fungal-dominated systems, the observed difference in aggregate stability may have been due to more rapid binding by fungal hyphae under FS, though no significant differences were observed in microbial biomass C (Figure 5.6). Although estimates of the microbial biomass by chloroform-incubation (CFI) was reported to be in a close 1:1 relationship with estimates of microbial biomass via microscopy (including direct counts of fungal and bacterial cells) in the original work (Jenkinson et al., 1976), the CFI method has failed to efficiently extract fungal biomass from some forest soils (Ingham et al., 1991). In their work, microscopic estimates of microbial biomass in both ectcomycorrhizal mats and non-mat forest soils were 10-300 times greater compared to the CFI method, the difference between the methods being greater for the ectomycorrhizal mats. Other work, however, has shown sensitivity of the CFI method to the use of fungicides, since both microbial biomass C and fungal hyphae lengths significantly decreased after application of fungicide to a mixed meadow that had been recently plowed at HSB (Hu et al., 1995).

Beyond the change is aggregate stability, a significant increase in total SOC from the starting concentration (0.92%) to the mean concentration after one year (1.08%) was also observed from 0-5 cm under FS. This increase in SOC in the three FS plots where 0-5 cm C concentrations exceeded the initial SME total SOC concentration could, however, be explained by mixing of a relatively small portion of the native FS soil (9-22%) with the SME soil. On the other hand, the increase in SOC, which is equivalent to an increased storage of 1 Mg C ha^{-1}, could result partly from input of DOC in litter leachate, although these inputs are small (Devine, 2009, Table 3.4) or possibly from annual fine root production that has been reported to range from 250-8,200 kg C ha^{-1} yr^{-1} (Nadelhoffer and Raich, 1992).

Finally, decreases in SOC compared to the initial concentration from 5-15 cm under all three land uses suggest the importance of macroaggregate stability for the protection of SOC. This reduction occurred even though the soil used in the moving experiment was CT soil in which macroaggregate protection of SOC had already been impacted during 30 years of continuous moldboard plowing.

Conclusions

Changes in aggregate size distributions after 30 years of different agricultural management were only clearly evident to a depth of 5 cm between conventional tillage (CT) and no-till (NT) systems. When adjacent land undergoing forest succession (FS) was added to the comparison, structural changes were evident to 28 cm. Changes in SOC concentration and composition occurred along with changes in structural stability to a depth of 15 cm, supporting the general notion that tillage reduces the capacity of soil to physically protect organic matter from decomposition. Although differences in stability were evident from 15-28 cm, no significant difference in SOC concentration was observed among the land uses, suggesting that the stability metric (dry-sieved MWD/wet-sieved MWD) is not necessarily linked to an increase in the capacity to protect SOC from decomposition. SOC results lend support to two different models of how SOC becomes physically protected in systems lacking mechanical disturbance, one that highlights the importance of particulate organic carbon (POC) and the other dissolved organic carbon (DOC). Since POC contributed close to half of the differences in SOC differences between land uses, it is possible that micro-scale fluxes of DOC are also playing an important role in maintaining higher fine-C concentrations in soils with greater pore connectivity, such as the NT and FS soils in this study. The importance of macroaggregate stability for the protection of SOC was also demonstrated by the destruction of large macroaggregates in a soil moving experiment in which losses of carbon from 5-15 cm were observed under all land uses. The SME experiment also demonstrated that the recovery of water-stable macroaggregates can be rapid, since significant increases in stability under FS were observed in the experiment to 15 cm, although the short-term role in C increase was uncertain.

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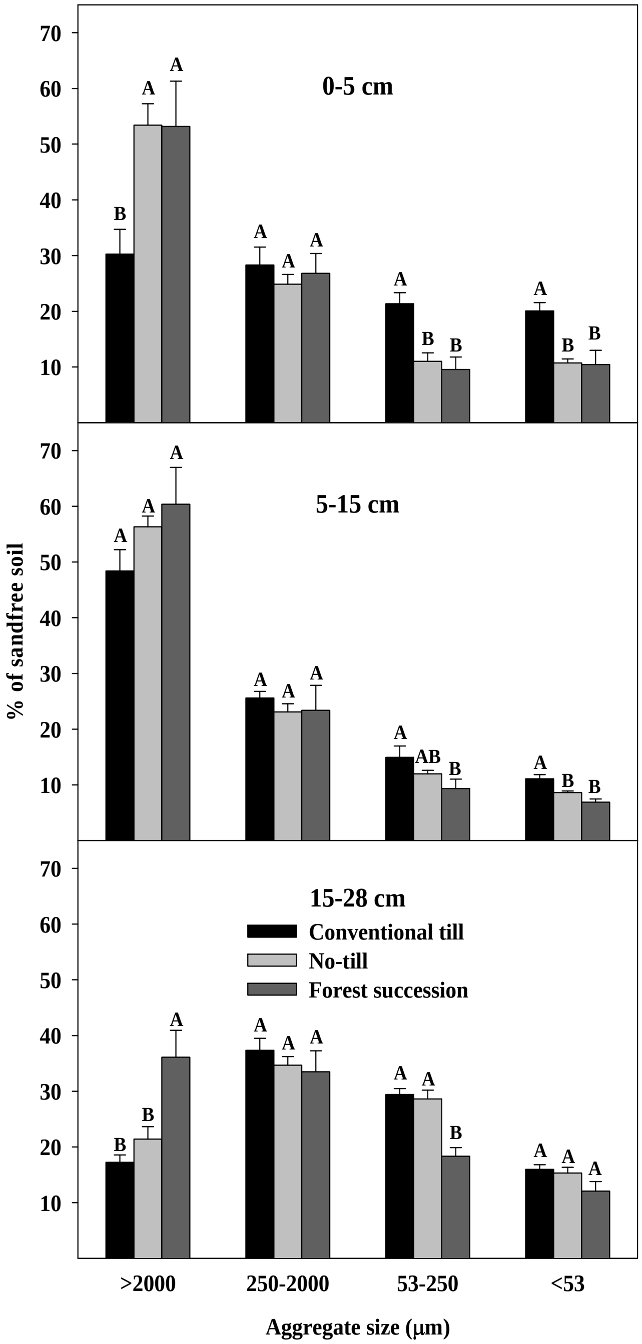

Figure 5.1. Percent sand-free soil mass (mean ± 1 SE) in four sand-free aggregate size fractions at the Horseshoe Bend Agroecosystem Experiment (n=4), Athens, GA, USA, October 2007. Different letters within an aggregate size class and depth class represent a significant difference between land uses (α=0.1).

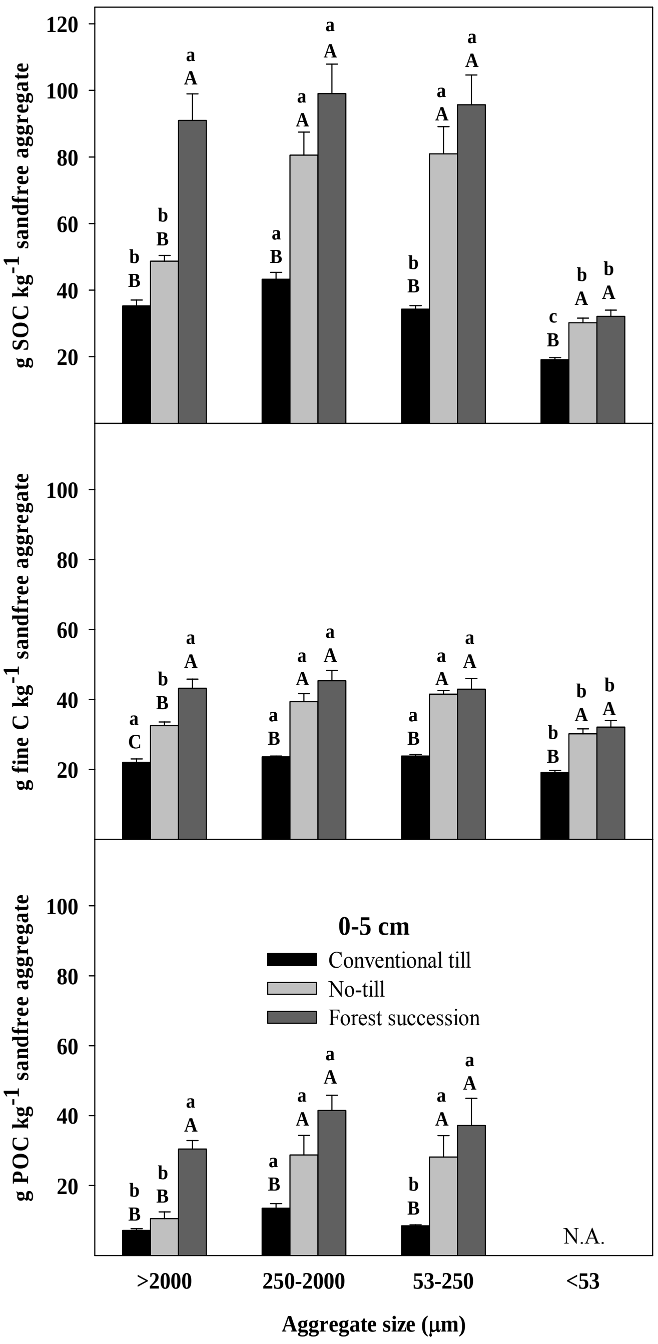

Figure 5.2. Total soil organic C (SOC), fine C (<53 µm), and particulate organic C (POC) (53-2000 µm) concentrations on a sand-free basis from 0-5 cm in four different aggregate size fractions (mean ± 1 SE) in the Horseshoe Bend Agroecosystem Experiment (n=4) Athens, GA, USA, October 2007. Different uppercase letters within an aggregate size class and depth class represent a significant difference between land uses. Different lowercase letters within a depth class and a land use represent a significant difference among aggregates size classes (α=0.1).

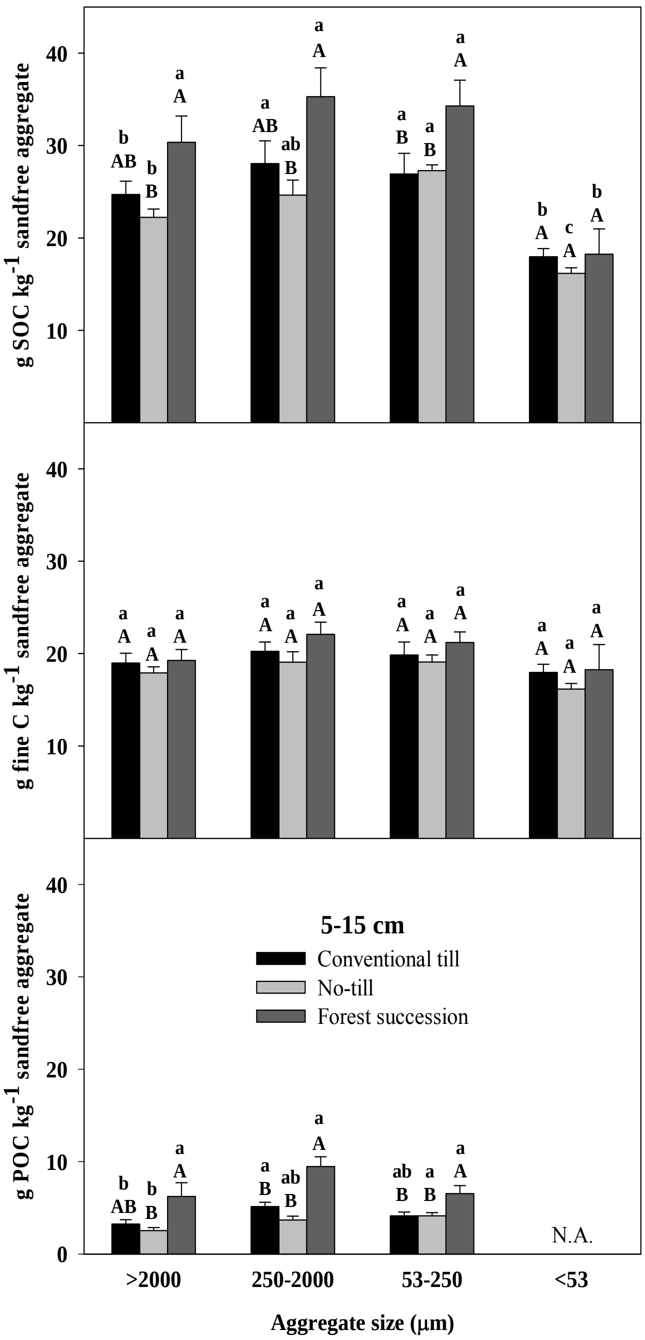

Figure 5.3. Total soil organic C (SOC), fine C (<53 μm), and particulate organic C (POC) (53-2000 μm) concentrations on a sand-free basis from 5-15 cm in four different aggregate size fractions (mean ± 1 SE) in the Horseshoe Bend Agroecosystem Experiment (n=4) Athens, GA, USA, October 2007. Different uppercase letters within an aggregate size class and depth class represent a significant difference between land uses. Different lowercase letters within a depth class and a land use represent a significant difference among aggregates size classes (α=0.1).

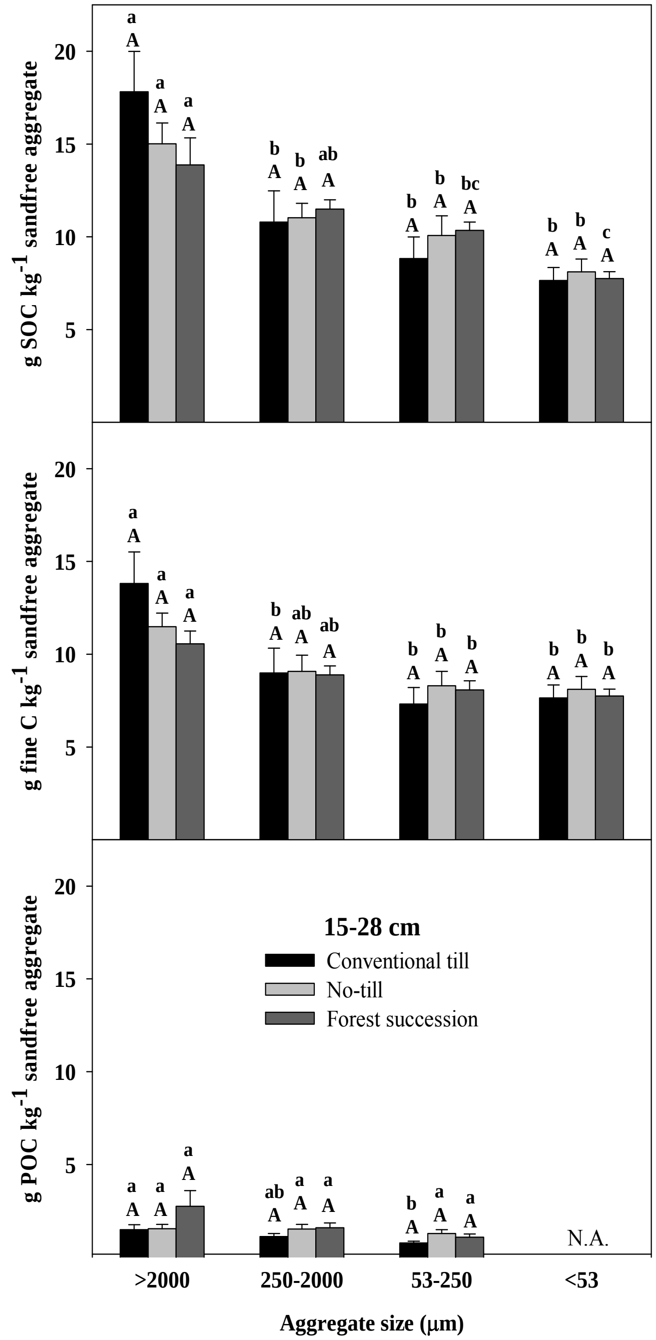

Figure 5.4. Total soil organic C (SOC), fine C (<53 μm), and particulate organic C (POC) (53-2000 μm) concentrations on a sand-free basis from 15-28 cm in four different aggregate size fractions (mean ± 1 SE) in the Horseshoe Bend Agroecosystem Experiment (n=4) Athens, GA, USA, October 2007. Different uppercase letters within an aggregate size class and depth class represent a significant difference between land uses. Different lowercase letters within a depth class and a land use represent a significant difference among aggregates size classes (α=0.1).

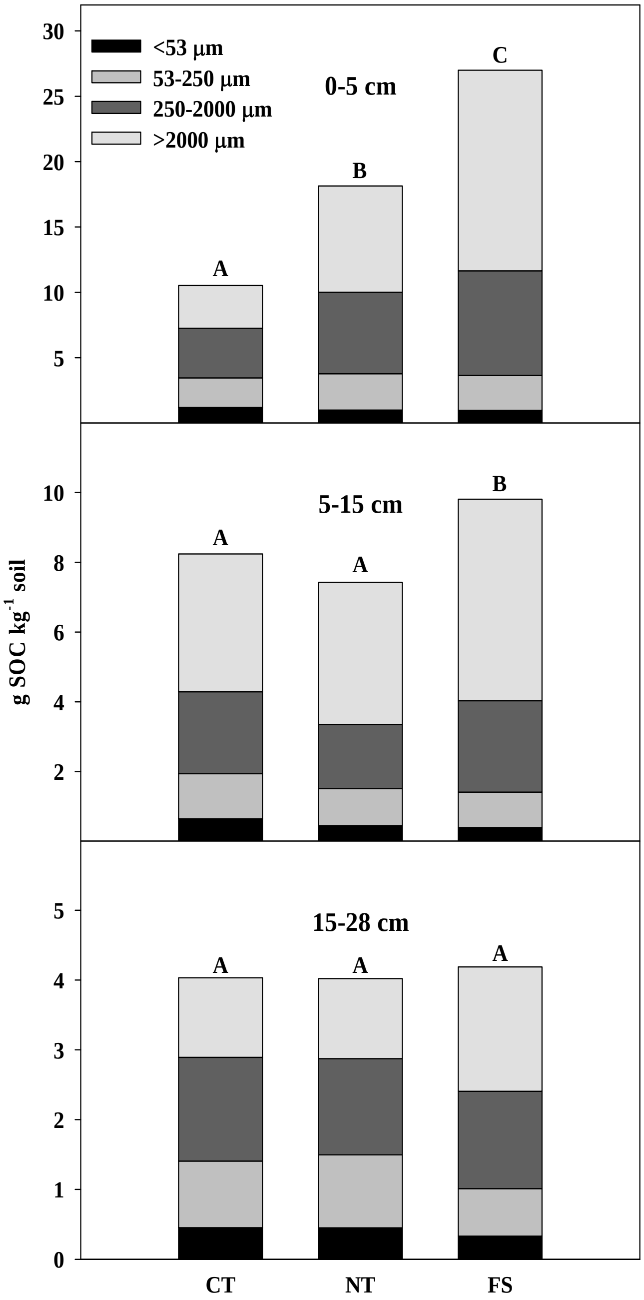

Figure 5.5. Contributions of four different aggregate size fractions to total soil organic C (SOC) concentrations. Different letters indicate a significant difference between land uses in a depth class (α=0.1). Means of the sums of the four fractions are shown (n=4) from Horseshoe Bend, Athens, GA, USA, October 2007.

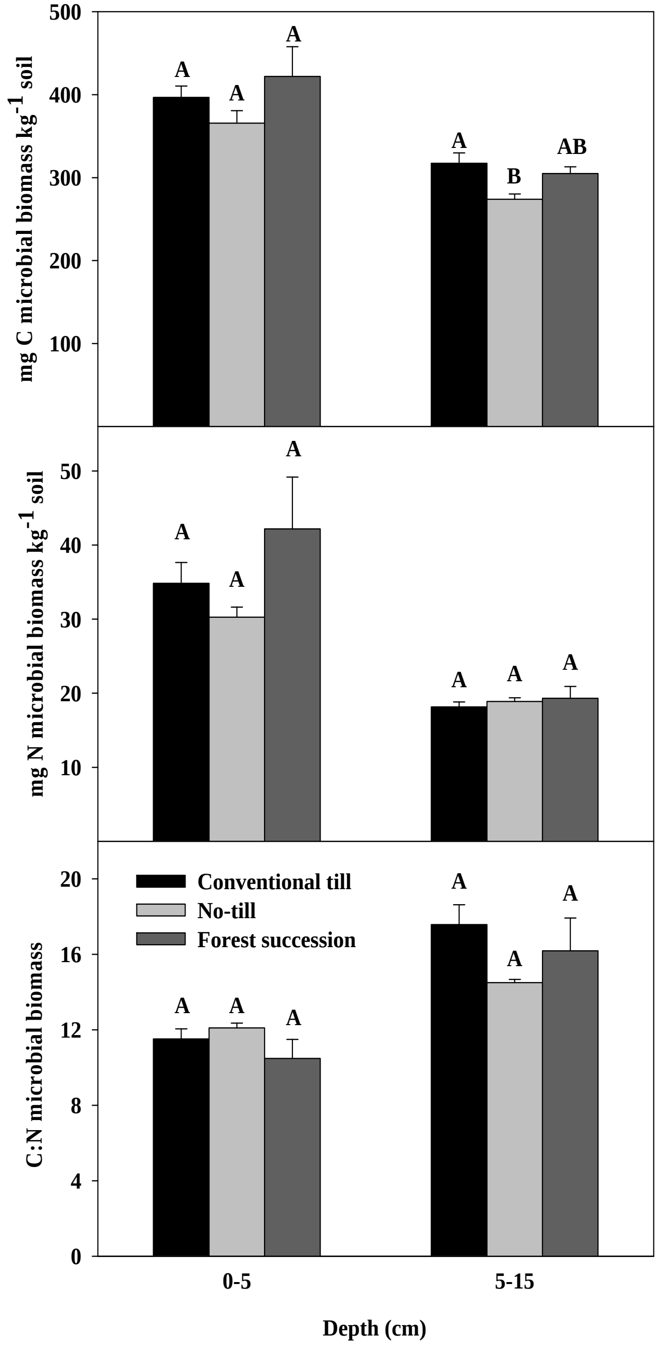

Figure 5.6. Microbial biomass C, N, and C:N (mean ± 1 SE) at the end of the soil moving experiment (n=4). Conventional till soil was initially dried and crushed to pass a 1 mm sieve and then installed under the three different land uses for a period of one year at Horseshoe Bend, Athens, GA, USA, July 2007-August 2008. Different letters within a depth class represent a significant difference between land uses (α=0.1).

Table 5.1. Aggregate stability (mean ± 1 SD) at two depths at the end of a soil moving experiment (n=4). Conventional till soil was initially dried and crushed to pass a 1 mm sieve and then installed under three different land uses for a period of one year at Horseshoe Bend, Athens, GA, USA, July 2007-August 2008. Different letters indicate statistical significance among treatment means within a depth class based on Tukey's HSD with $\alpha=0.1$ (lowercase) or $\alpha=0.05$ (uppercase).

Depth	*Land use*	*Dry MWD*[†]	*Wet MWD*	*Stability index*
cm		-----------mm-----------		Wet/Dry
0-5	Conventional Till	4.3 ± 0.4^{ab}	1.4 ± 0.2^{a}	0.33 ± 0.06^{a}
	No-Till	4.5 ± 0.3^{a}	1.9 ± 0.3^{b}	0.43 ± 0.09^{a}
	Forest Succession	3.9 ± 0.3^{b}	3.1 ± 0.2^{C}	0.79 ± 0.03^{B}
5-15	Conventional Till	4.8 ± 0.6^{a}	1.2 ± 0.2^{a}	0.26 ± 0.08^{a}
	No-Till	4.8 ± 0.6^{a}	1.0 ± 0.2^{a}	0.22 ± 0.05^{a}
	Forest Succession	3.6 ± 0.5^{B}	2.1 ± 0.3^{B}	0.60 ± 0.10^{B}

[†] Mean weight diameter

Table 5.2. Total soil organic C (SOC), N and C:N ratios (mean ± 1 SD) at two depths at the end of a soil moving experiment (n=4). Conventional till soil was initially dried and crushed to pass a 1 mm sieve and then installed under the three different land uses for a period of one year at Horseshoe Bend, Athens, GA, USA, July 2007-August 2008. Different letters indicate statistical significance between treatment means within a depth class based on Tukey's HSD with α=0.1 (lowercase) or α=0.05 (uppercase).

Land use	*depth*	*SOC*	*soil N*	*C:N*
	-cm-	--------g kg^{-1} soil-------		
Initial	2.5	9.2 ± 0.2	0.81 ± 0.04	11.4 ± 0.4
Conventional till		9.1 ± 0.3^{A}	0.77 ± 0.04^{a}	11.9 ± 0.4^{A}
No-till		8.7 ± 0.2^{a}	0.76 ± 0.02^{a}	11.5 ± 0.1^{A}
Forest succession		10.9 ± 1.7^{B}	0.87 ± 0.13^{a}	12.6 ± 0.3^{b}
Initial	10	9.2 ± 0.2	0.81 ± 0.04	11.4 ± 0.4
Conventional till		8.3 ± 0.2^{a}	0.71 ± 0.03^{a}	11.6 ± 0.2^{a}
No-till		8.3 ± 0.2^{a}	0.73 ± 0.02^{a}	11.3 ± 0.2^{b}
Forest succession		8.4 ± 0.6^{a}	0.73 ± 0.06^{a}	11.5 ± 0.1^{ab}

Table 5.3. Estimated mixing of native forest soil and initial soil moving experiment (SME) soil. Predicted aggregate stability is a weighted average of mixing 100% stable native forest with the agroecosystem 0-5 cm soil at the end of the SME (aggregate stability =0.38). Initial soil organic C (SOC) = 9.2 g kg^{-1} soil and initial soil N = 0.81 g kg^{-1} soil. Horseshoe Bend, Athens, GA, USA, July 2007-August 2008.

Plot	*Native*	*SME*	*Native*	*SME*	*Mixing of native*	*Predicted aggregate stability*
	-g SOC kg^{-1} soil-		-g N kg^{-1} soil-		---%---	Wet/Dry
E	21.2	11.2	1.38	0.91	16.3	0.48
N	26.3	13.1	1.85	1.02	22.4	0.52
S	19.5	10.2	1.39	0.82	8.9	0.44
W	22.8	9.1	1.57	0.71	0	0.38

Table 5.4. The proportion of particulate organic carbon (POC) within aggregate fractions and whole soil (mean ± 1 SD) at Horseshoe Bend, Athens, GA, USA, October 2007.

Land use	*Depth*	*Large macroaggregates*	*Small macroaggregates*	*Microaggregates*	*Whole soil*[1]
	--cm--	----------------------------------% POC----------------------------------			
CT	0-5	20.2 ± 1.3^{a}	31.0 ± 4.2^{a}	24.7 ± 0.6^{a}	22.6 ± 0.9^{a}
NT		21.3 ± 6.3^{a}	34.8 ± 7.9^{ab}	33.7 ± 7.3^{ab}	26.9 ± 6.6^{a}
FS		33.8 ± 5.7^{b}	41.8 ± 4.6^{b}	38.1 ± 9.8^{b}	35.5 ± 5.1^{b}
CT	5-15	13.0 ± 2.4^{ab}	18.4 ± 1.9^{a}	15.3 ± 1.2^{a}	13.8 ± 1.8^{a}
NT		11.4 ± 2.6^{b}	14.9 ± 2.6^{a}	15.0 ± 2.2^{a}	12.1 ± 2.3^{a}
FS		19.7 ± 6.4^{a}	26.9 ± 4.7^{b}	18.8 ± 2.0^{b}	20.4 ± 5.1^{b}
CT	15-28	8.2 ± 0.9^{a}	10.4 ± 1.2^{a}	8.8 ± 0.8^{a}	8.2 ± 0.5^{a}
NT		10.1 ± 2.0^{a}	13.6 ± 2.8^{a}	12.5 ± 1.9^{b}	10.8 ± 1.2^{ab}
FS		20.0 ± 13.6^{a}	13.7 ± 3.5^{a}	10.3 ± 2.7^{ab}	15.1 ± 6.7^{b}

[1] Calculated by summation of individual fractions

CHAPTER VI

CONCLUSIONS

Results from this thesis clearly demonstrate the effects of land use on soil properties and biogeochemical cycles and show that forest succession (FS) has a more dramatic effect than a difference in agricultural management (no-till (NT) vs. conventional tillage (CT)) at Horseshoe Bend (HSB). In the case of carbon (C) storage, FS has led to a large accumulation of aboveground C in biomass that overshadows the relatively small increase in soil organic carbon (SOC) relative to the CT soil profile (0-2 m). The difference in SOC is mostly associated with increases in particulate organic carbon (POC), possibly reflecting root growth as the source of SOC change, especially at depth. Three decades of NT agriculture has led to a similar increase in SOC compared to CT that is mostly associated with a more finely divided fraction of C (<53μm). It is surprising that the return of the annual net primary production in the form of crop residues under NT has not led to a corresponding increase in SOC compared to FS. This means that SOC is decomposed at a faster rate under NT compared to FS but can eventually become stabilized in the form of fine C. Soil structure has also been altered to depths previously not studied at HSB. The maintenance of water-stable aggregates near the surface of FS and NT may be the primary mechanism for the increase in SOC. The increase in stability under FS may be linked to the increase in POC from 0-15 cm but has not led to a significant increase from 15-28 cm in either total SOC or POC. As has been shown in previous research, differences in CT and NT were limited to the 0-5 cm depth class. The soil moving experiment clearly showed that such alterations under FS can occur as rapidly as a year and that macroaggregation does afford protection of SOC from decomposition in the field under all land uses.

Associated with the increase in forest biomass is a large transfer of base cations from the soil exchangeable pool that is one of the factors in the observed soil acidification under FS. Lack of liming to the forest could explain the increase in exchangeable acidity relative to CT and NT. When estimated forest uptake of magnesium (Mg) and potassium (K) is added to the forest soil exchangeable pool, this exceeds the agroecosystem exchangeable pool minus the quantity of Mg and K in fertilizer applied to the agroecosystem. This suggests leaching losses of Mg and K have been greater under CT and NT, a conclusion which is supported by past and current soil solution monitoring. The results are less clear in the case of exchangeable soil calcium (Ca), since fertilizer applications and forest uptake do not account for the currently observed differences between the FS and agroecosystem profiles. An underestimation of Ca uptake by the forest is the most likely cause for this result.

APPENDIX A

HYDROLOGICAL MODEL DESCRIPTION

The goal of estimating hydrologic fluxes was not to separate treatment effects on water flow through the soil but to scale concentration data from lysimeters to a field-scale flux. Potential evapotranspiration (PET) was estimated during the period of the long-term HSB agroecosystem experiment (Jan 1977- Jul 2008) on a monthly basis and on a daily basis during the monitoring period of this work (1-Aug 07 to 31-Jul 08) using a software program called the ETo Calculator (Raes and Munoz, 2008) that employs the calculation procedure described in Allen et al. (1998) and is based upon the Penman-Monteith method. For the long-term estimation, latitude, longitude, elevation, and monthly mean and minimum temperatures were used as input variables; for the shorter monitoring period PET estimates, latitude, longitude, elevation, daily mean and minimum temperatures, mean wind speed, and relative sunshine hours estimated from average sky cover were used as input variables. All climactic data were downloaded from the Athens Ben Epps Airport (33°57' N, 83°20' W) data set available through the National Climactic Data Center (NCDC, 2007) or from preliminary data available through the National Weather Service (NWS, 2008). The ETo software program employs procedures to estimate missing humidity, wind, and radiation data required by the Penman-Monteith method (Allen et al., 1998). Since PET is known to vary widely in the southeastern US based upon the calculation method (Lu et al., 2005), the Thornthwaite method was also used to estimate PET over the same time periods, for which all data was available. Since this method produces PET estimates on a monthly time step, we scaled the Thornthwaite results to a daily estimate by using the daily distribution provided by the Penman-Monteith method in order to make a comparison between PET methods during the shorter time period (1-Aug 07 to 31-Jul 08). Precipitation data from weekly collections at HSB was distributed on a daily basis according to daily precipitation data from the Athens Ben-Epp dataset. Infiltration was estimated from an overall linear regression for all treatments between litter leachate collections and precipitation, which was divided into two seasons (Figure I.1). For the long-term model, monthly infiltration was estimated using the same linear regressions by season. The model began January 1977, but average fluxes reported in the results are based on the 1978-2007 annual fluxes, so as to give the model profile time to equilibrate. An output file of soil tensions in the 1 m profile at the end of Dec-2006 was used as the initial conditions for the short-term model that began 1-Jan 2007. Root uptake and vertical water movement through a 1 m soil profile were then estimated with a one-dimensional model created in HYDRUS (2D/3D) version 1.02 (Simunek et al., 2007) using the estimated PET and infiltration as input data. The 1 m model profile was divided into five layers to match the soil depth classes described previously, which were discretized into 1 cm vertical increments. Soil hydraulic parameters (θ_r, θ_s, α, n, and K_s) for each layer were estimated from across treatment averages of textural and bulk density data via neural network prediction using the Rosetta Lite v.1.1 tool that accompanies HYDRUS (2D/3D) (van Genuchten, 1980). Modeled actual evapotranspiration was based on the Feddes water uptake reduction model with parameters based on *Zea mays* and taken from a database that accompanies HYDRUS (2D/3D). This allows for a reduction of actual root water uptake relative to PET, depending upon soil matric tension. Roots were assumed to be present to 1 m with a depth of maximum intensity at 0 cm, decreasing with depth according to a published function with P_z=3 (Vrugt et al., 2001) that also accompanies HYDRUS (2D/3D). Generation of an internal mesh-line available in

HYDRUS (2D/3D) at 15 cm depth allowed for estimation of a water flux at 15 cm (Simunek et al., 2007). HYDRUS (2D/3D) automatically generates an output file for various boundaries, which allowed for estimation of the water flux at 100 cm depth, the free drainage boundary in our model. Finally, while we did not have rigorous, quantitative means by which to either calibrate or verify our model, we graphed modeled soil tensions at both 15 cm and 100 cm to see how they matched lysimeter collections in the field. Based upon the tension established in the lysimeter, field collections are theoretically obtainable when soil matric tensions reach approximately -650 cm at both depths (Figure 4.14).

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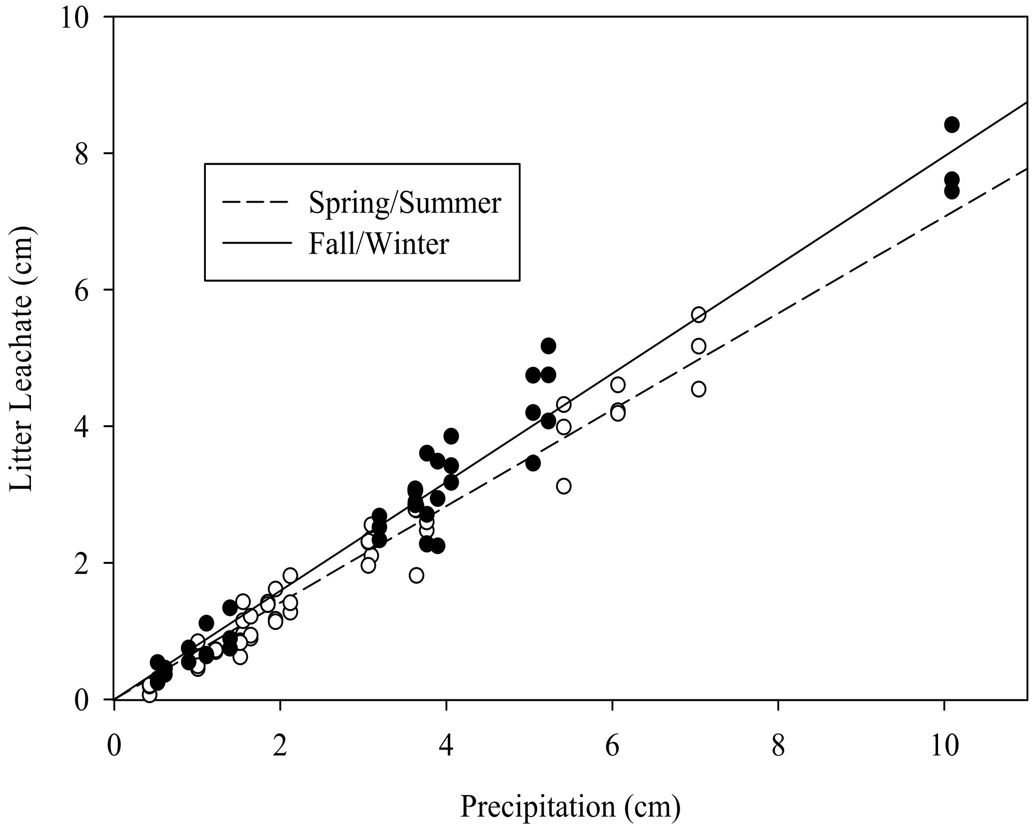

Figure A.1. Linear regressions of weekly precipitation vs. litter leachate collections across land use at Horseshoe Bend, Athens, GA, August 2007-July 2008, demonstrates a consistently proportional relationship, independent of the weekly rainfall. For spring/summer (open circles), $y=0.707(x)$, $r^2=0.95$ and for fall/winter (closed circles), $y=0.795(x)$, $r^2=0.96$, where x=rainfall and y=litter leachate.