AGGREGATE ORGANIC CARBON IN NORTH FLORIDA SLASH AND LOBLOLLY PINE ECOSYSTEMS

By

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To my parents who inspired, allowed and encouraged me to follow my goals since childhood.

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LIST OF ABBREVIATIONS

ADEC	Aggregate Dispersion Energy
AOC	Aggregate Organic Carbon
C	Carbon
DOC	Dissolved Organic Carbon
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
Mid-IR	Mid-Infrared
SOM	Soil Organic Matter
SOC	Soil Organic Carbon
TOC	Total Organic Carbon

Abstract of Thesis Presented to the Graduate School
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It's been found that of the estimated 4,110 GT of carbon (C) found in the world's C cycle approximately 38% can be found in the soil. There has been a growing interest in C sequestration through improved soil management practices. Aggregation is a process by which C can be physically protected by encrustation. Sandy surface horizons, which have been thought of as weak structure, have been previously found to have small aggregates with upwards of 50% soil organic C (SOC) contained in those aggregates. This study targets pine ecosystems under the two dominant species in the southeast US, which are loblolly pine (*Pinus taeda*) and slash pine (*Pinus elliottii*). The objectives were to *a)* validate ultrasonic methodology, *b)* to investigate soil aggregate energy at which SOC is held and determine if this is influenced by pine ecosystems of loblolly vs. slash; *c)* determine if aggregate dispersive energy is a controlling factor in aggregate organic C (AOC) turnover; and *d)* determine the chemical fingerprint of AOC as aggregate dispersive energy increases within species ecosystem. The data show that soil under slash pine was slightly better aggregated with 4.1% more AOC as a percentage of TOC. However, loblolly had 33% more AOC (g g^{-1}soil) than did slash.

Incubation and mid-infrared (mid-IR) results showed that there was no discernable difference in AOC held at different energy levels. On the other hand, SOC was influenced by pine species. Slash pine soils were higher in aliphatic C and had higher specific mineralization rate; while loblolly was higher in aromatic C. These results are the first contrast of SOC under these two species. It suggests that loblolly management, as normally practiced by landowners, will store more soil C; yet that soil C will not be protected from mineralization by soil aggregation.

CHAPTER 1
INTRODUCTION TO AGGREGATE ORGANIC CARBON

Of the estimated 4,110 GT of C found in the world's C cycle approximately 38% can be found in the soil (Leu, 2007). Moreover, soil organic C (SOC) is critical to soil processes as it affects water retention, soil structure, and nutrient cycling (Sanchez and Ruark, 1995). Soil C is protected by a variety of mechanisms including: physiochemical by sorption to clay; biochemical through formation of recalcitrant C compounds; physical via soil aggregation (Stone et al., 1993; Six et al., 2002; Blanco-Canqui and Lal, 2004); *chemical* by combining with metals such as aluminum; translocational by C moving to deeper soil horizons where decomposition is limited by either microbial populations or oxygen; and depositional under anaerobic/anoxic environmental conditions.

The architectural organization of sand, silt, and clay by organic compounds and inorganic cementing agents creates aggregates (Blanco-Canqui and Lal, 2004). An aggregate hierarchy in soils has been suggested where aggregates of different stability, often controlled by organic materials, can be classified (Oades and Waters, 1991). Three models have been used to explain soil aggregation and SOC (Blanco-Canqui and Lal 2004). The first was proposed by Tisdall and Oades (1982) and based on aggregate hierarchy. In this model, stage 1 is the binding of primary particles into microaggregates (53-250μm) where soil organic matter (SOM) is often the principal binding agent. Stage 2 is characterized by the formation of medium-sized microaggregates; while stage 3 encompasses the formation of large microaggregates and macroaggregates.

The second model was proposed by Oades (1984) which was a revision of the above mentioned model where macroaggregates form first and microaggregates are created afterward. The third model, developed by Six et al. (2000), begins with the formation of macroaggregates created by the binding of organic residues. This is followed by intra-aggregate particulate OM stabilizing these macroaggregates. The next stage is the formation of microaggregates encrusted by fine organic particles. Finally, stable microaggregates are formed by the degradation of macroaggregates.

Aggregate formation depends on factors that develop aggregate stability. Soil aggregation depends on changes in water status, freezing or thawing, tillage, movement of large biota (plant roots, earthworms and macro fauna) and clay content (Oades and Waters, 1991). Roots, fungal hyphae, and polysaccharides that are intimately associated with the mineral fraction appear to be important stabilizing agents (Kay, 1997). A study on macroaggregate stability showed that hyphae are linked to aggregation in sandy soils (Degens et al. 1996). It is often assumed that SOC within aggregates is not available to microbial decay, and as a consequence the greater the stability of the aggregate against dispersion leads to greater protection of the SOC. Studies have shown mixed results when investigating the relationship between aggregate tensile strength and SOC (Blanco-Canqui and Lal, 2004). A strong correlation was found by Golchin *et al*. (1995) between particulate organic matter and stability of 1-2 mm macroaggregates (increasing SOC increases aggregate stability); while Chaney and Swift (1984) found a high correlation between aggregate stability, SOM, total carbohydrate, and humic material. Conversely, Jastrow *et al.* (1998) found a poor correlation between SOC and aggregate sizes.

The purpose of this thesis was to investigate soil C and soil aggregation in very sandy soils supporting southern pine plantations. In Florida, pine lands made up almost exclusively of slash pine (*Pinus elliottii)* and loblolly pine (*Pinus taeda)*, cover 1,252,569 ha of which 30% (371,481 ha) are in conservation areas or managed areas; 56% (702,182 ha) are in private ownership. The remaining 14% encompasses private lands in conservation programs (FFWCC, 2005). Spodosols cover 27% of Florida's area (Stone et al., 1993). Florida Spodosols contain 0.05% of the global C pool only on approximately 0.028% of the total land area (Stone et al., 1993). Within our sampling study area, pinelands represent 25% of the land cover. Florida's sandy surface soils are not known for their ability to store C due to their weak structure and low clay content (Carlisle et al., 1981, 1988, 1989) resulting in a low ability to physiochemically protect C from microbial decomposition.

The few studies that have investigated aggregation in Southeastern Coastal Plain sandy soils have shown that surface soil aggregation is dominated by microaggregates over macroaggregates. The 'weak soil structure' of these soils implies poor aggregation, yet Sarkhot et al. (2007a) have shown aggregate hierarchy with at least 50% of the total C found in aggregates (Sarkhot et al., 2007a). However, the degree of protection provided by soil C in Lower Coastal Plain sandy soils is unknown.

The overall purpose of this study was to investigate soil aggregate C as to its importance in forest land use and its role in SOC protection; it was addressed by investigating three principle objectives. The first objective of this research was to investigate the range in stability of soil aggregates in these sandy surface horizons and determine if ecosystem vegetation dominated by *P. taeda* vs *P. elliottii* influence the amount of SOC in aggregates and the strength of aggregates in which it is held. This is the focus of Chapter 2. Aggregate stability is the ability of the soil to retain its arrangement of solid and void space when exposed to stress (Kay, 1997). Due to the low content of clay (<2%) and the sandy nature of North Florida Spodosols, aggregation it thought to have low capabilities to physically protect SOC from microbial decomposition. However, aggregate stability has been found to occur in Florida's surface soils (Sarkhot et al., 2007a) and is found to be proportional to the energy required to disperse the aggregates via sonication. While this Chapter addresses the amount and type of aggregation, it does not investigate whether more stable aggregates provide superior protection to SOC from microbial use.

This thesis's second objective was to determine if aggregate dispersive energy (a measure of stability) is a controlling factor in aggregate organic C (AOC) turnover in sandy soils (Chapter 3). By dispersing aggregates at different energies and then mineralizing the SOC, this objective tested the hypothesis that SOC held at higher dispersive energies is better protected against decomposition. When all soil aggregates are dispersed, a higher rate of mineralization would be expected if aggregates do protect SOC.

The third and last objective (Chapter 3) was to determine if the chemical characteristics of SOC and AOC are different between slash and loblolly ecosystems; and as aggregate dispersive energy increases. Qualitative analysis of SOC functional groups was analyzed by a form of Fourier-transformed infrared reflectance spectroscopy (FTIRS) called DRIFTS (Diffuse Reflectance Infrared Fourier Transformed Spectroscopy). Fourier transform infrared spectroscopy is a cost effective, time saving, non-destructive and environmentally sound technique of soil analysis (Dunn et al., 2002); while Boehm titrations provide qualitative and quantitative information on soil functional groups (Radovic et al, 2003).

Chapter 4 is a summary of this thesis and attempts to encapsulate the salient points presented in the preceding chapters as well as identify the continuing gaps in knowledge and suggest future research directions.

CHAPTER 2
SOIL AGGREGATE STABILITY AND ITS INFLUENCE ON CARBON IN PINE ECOSYSTEMS IN NORTH FLORIDA

A soil aggregate is a group of soil particles that cohere more strongly to each other than to other adjoining particles (Sylvia et al., 2005). In Florida's sandy soils, organic matter (OM) is the dominant input that leads to the formation and stabilization of soil aggregates, which in turn may protect soil organic C (SOC) from microbial decomposition (Lal et al., 1997). Soil organic matter influences the formation, stabilization, and degradation of soil aggregates and is the major aggregate binding agent that generates aggregate hierarchy (Tisdall and Oades, 1982; Oades and Waters, 1991). Aggregates assist in the reduction of erosion, in the improvement of infiltration and in the movement of water. They can also affect plant growth.

Different theories have been suggested about aggregates and their capability to protect C. Tisdall and Oades (1982) determined that the age, size and stability of an aggregate is a function of organic agents: transient agents decompose rapidly and are associated with aggregates larger than 250 um; temporary binding agents are associated with OM that comes from vesicular-arbuscular (VA) mycorrhizal hyphae (Tisdall and Oades, 1979) and persist for months or years; and persistent agents are resistant aromatic components. Soil microorganisms can promote soil aggregation through the production of polysaccharides, glomalin and hyphae (Sylvia et al., 2005). It has been shown that more labile OM is tied up in macroaggregates (2000-250 µm) and more decomposed OM is tied up in microaggregates (<250 µm) (Six J et al. 2001). Puget et al. (1995) also suggested that the organic C concentration increased with aggregate size, and that organic C is more labile in micro than in macroaggregates. This was supported by a study where the microbial biomass and activity in soil aggregates was higher in macroaggregates than in microaggregates for native prairie soils (Gupta and Germida, 1988). However, other theories support the idea of “encrustation of SOM” inside microaggregates providing the protection that result in SOC sequestration (Tisdall and Oades, 1982; Golchin et al., 1994; Jastrow and Miller, 1996).

The capacity of OM incorporation into aggregates has most often been estimated from the soil clay and silt content (Hassink et al., 1997); however, using sound waves to disrupt the aggregates has also been employed by others (North 1976; Christensen 1992; Cambardella and Elliot, 1993; Six et al., 2001; Swanston et al., 2005; Sarkhot et al. 2007a). Aggregate dispersion energy curves (ADEC) have been used to examine aggregate strength and determine the quantity of C in aggregates held at different dispersion energies. This method quantifies the physically protected C (Sarkhot et al. 2007a; North, 1976; Christensen, 1992; Cambardella and Elliot, 1993; Six et al., 2001; Swanston et al., 2005). Through this methodology Sarkhot et al. (2007a) found evidence that suggested aggregate hierarchy in Florida’s sandy soils.

The overall purpose was to investigate the role that aggregation plays in C incorporation and sequestration in the surface sandy soils of the lower coastal plain supporting southern pine. This was addressed by focusing on two objectives. The first objective was to validate a sonication method that has been previously used to look at aggregate dispersive energy (Sarkhot et al., 2007a). While the method has been used as noted above, a detailed look at aggregate size and disappearance had not been made.

The second objective was to investigate the amount of SOC incorporated into aggregates in surface sandy soils; and determine if there was a difference due to growing loblolly or slash pine ecosystems.

Methodology

Experimental Site for Validation of the Sonication Method

The study site was located 10 km north of Gainesville, FL on a flat topography (<2% slope) within a forest plantation growing on a Pomona fine sand (sandy siliceous hyperthermic Ultic Alaquod). The climate of the region is a hot and humid with an average yearly precipitation 113.3 cm, and yearly average minimum and maximum temperatures of 14 and 27° c respectively (southeast regional climate center, 2010).

The study design has previously been describe in detail since it has been a subject of multiple soil and above-ground investigations (Colbert et al. 1990; Dalla-tea and Jokela, 1991; Jokela and Martin, 2000; Martin and Jokela, 2004); but is briefly described here. In 1983, *P. elliottii* and *P. taeda* seedlings were planted at a1.8 x 3.6 m spacing in a 2x2x2 factorial design employed in three blocks. Only one pineland block was sampled. The method was evaluated on soil from two depths: 0-5cm and 5-10cm. (The first letters of principal words must be capitalized).

Experimental Sites for Stability Levels, Mineralization and Chemical Analysis

The experimental sites were primarily chosen from a previous stratified random sampling plan for a large scale research project with the objective of developing a soil C inventory of the state of Florida (Myers unpublished data), designed to proportionally sample sites relative to the area's land use pattern. The study area is the USDA Conservation Area 2 in North Florida. From this sampling plan 13 sites were selected.

Seven sites supported a loblolly pine plantation and 6 sites supported slash pine plantations. The sites were chosen so that they represented the mean and the range of soil C reported in the larger data set. “The pinelands category includes north and south Florida pine flatwoods, south Florida Pine rocklands, and commercial pine plantations […]”(FFWCC, 2004).

Soil samples were collected at the sampling locations with 4 cylindrical metal cores of 20 x 5.8 cm on the surface soil. Samples were measured for bulk density and moisture content then air-dried and dry-sieved to soil samples less than 2 mm (Myers et al., unpublished data). All study sites are Spodosols (Aquods). Samples were located in the north Florida counties of Alachua, Citrus, Clay, Duval, Flagler, Lafayette, St. Johns, Putnam, Taylor, and Volusia (Table 2-1).

The sampling sites were located on flatwood landscapes; which are predominantly somewhat-poorly to poorly-drained soils with a seasonally high water table. Loblolly and slash ecosystems had a common understory of saw palmetto (S. s*erenoa repens Small*), wax myrtle (*myrica cerifera* L.), gallberry (*ilex glabra* L.), brakenfern (*pteridium aquilinum* L.), blackberry (*rubus sp*.), fetterbush (*Lyonia lucida* Lam.); various grasses such as bluestem (*Andropogon virginicus* L.) and wiregrass (*Aristida beyrichiana*); and young oaks (*quercus sp*.) like water oak (*Quercus nigra* L.); also sweetgum (*liquidambar styraciflua* L.), bays (*persea sp*.), and Florida maple (*acer barbatum*). Both loblolly and slash ages range from 10-20 years with most of them in a plantation setting. However, one loblolly and one slash pine site were natural pine ecosystems.

Laboratory Methods

Sonication method

Soil samples were air-dried in a greenhouse and then passed through a 2 mm sieve. They were dry-sieved through a horizontal mechanical shaker for 5 min at 75 rpm using 53-, 150-, and 250-μm sieves with 100 grams of dry soil at a time (Sarkhot et al., 2007a).

An ADEC was developed for one block, three curves by size fraction with three replications of each. Each ADEC was built by placing 10 five-gram subsamples into beakers with 100 mL of deionized water. Using a sonic dismembrator (Fisher Scientific, Model 500, Hampton, NH), immersing the sonic probe 10 mm below the surface of the water, and applying an energy level. Energy levels from 0 to 200 j mL^{-1} were applied by using a range of amplitude (20-69%) and time (1-7 min) combinations. A correction factor, as described by Sarkhot et al. (2007a), was applied. Temperature rise was controlled by a pulse method (60 s on and 30 s off) (Sarkhot et al. 2007a). In this manner aggregates in each size fraction were incrementally disrupted. After disruption, each sample was passed through the same-sized sieve used to obtain the size fraction. The SOC remaining on the sieve after each sonication represented particulate SOC (POC) and aggregate OC (AOC) that resisted dispersion. The SOC passing through the sieve was considered the AOC that was dispersed by sonication. Sieve retentive were dried in a forced-air oven to 65 to 70^0C.

Three 0.1 g subsamples of the retentive oven dried material were collected on the sieve, in turn, placed under a microscope and the numbers of aggregates were counted with the help of a 1cm x 1cm grid system.

ADE curves for pine ecosystems

Previous studies have investigated soil C by size fraction, so initial analysis for sonication validation of ADEC was completed by size fractions to be consistent with those studies (Oades and Waters, 1991; Roscoe et al., 2000; Six et al., 2001; Sarkhot et al., 2007a). After these preliminary studies it was decided to work on whole soils having the range of energy that was necessary to disperse aggregates and create the ADECs. Samples were dry-sieved through a horizontal mechanical shaker for 5 min at 75 rpm using a 53 μm sieve size with a 100 grams of dry soil (soil size < 2mm) at a time (Sarkhot et al., 2007a). Samples used were all larger than 53 μm and smaller than 2000 μm.

Each energy curve was made up of ten points at increasing dispersion energy levels until all aggregates had been broken down. The curve ranged from 0-153 j mL^{-1}' this last level was selected based on the sonication validation study described above, where up to 153 j mL^{-1} were required to break down most aggregates. In order to set up a sonic dismembrator it is necessary to supply amplitude (20-90%) and time (2-14 min). The pulse method (60 s on and 30 s off) utilized was to avoid high temperatures that could interfere in the measurement (Sarkhot et al., 2007a). The energy output applied by the sonic dismembrator was given in joules and was internally calculated by the software. Since the energy output of the machine was calculated for the electrical energy (using an internal voltmeter) the conversion of electrical to mechanical energy at the probe tip is not 100% efficient so the energy absorbed by the water was calculated. The energy dissipated into the suspension was calculated with a correction factor. This actual energy was calibrated calorimetrically with a Dewar vessel as shown by Schmidt et al. (1999).

Each of the 13 sites had three ADEC replicates. Five grams were weighed in a 250 mL beaker for each subsample and then the sample was placed on a 250 mL thermal container and the probe was maintained at a constant depth of 12 mm. 100 mL of DI water was added slowly avoiding formation of bubbles that could provide a disruption in the energy applied to soil. The thermal container was then placed in a sound box, with the probe always immersed at the same depth and avoiding touching any of the walls of the container. After each sub-sample had been sonicated, to separate the material and quantify the C released by the broken down aggregates and the C still in aggregate, the next procedure applied was wet sieving. The content in the Dewar vessel was poured onto a 53 micron sieve. The AOC and SOC remaining on the sieve and the SOC that passed through the sieve were measured using loss-on-ignition (LOI). It was assumed that the energy applied did not disrupt particulate plant material debris which could result in a transfer of C that does not originate from aggregate disruption. The great advantage of using an ultrasonic vibration method is that it provides the opportunity to quantify the amount of energy applied to the soil in suspension and then it is possible to quantify the C that comes from that specific aggregate stability level.

Statistical analysis

An SOC analysis was ran to determine the distribution of population and sample. Variables SOC%, pH and forest floor were log normal. Outlier analysis was run and then an ANOVA was utilized. In order to compare means between energy level and species (categorical variables) for AOC g g^{-1} and AOC as percent of SOC (dependent variables) an analysis of covariance (ANCOVA; STATISTICA 9.0, Stat soft, Inc.; Tulsa OK) procedure was used for each dependent variable. The covariate, TC was utilized to account for the variability that occurred between the sampling sites. Sampling distributions were log normal both for AOC (g g^{-1} soil) and AOC as a percent of SOC (AOC %), but for the purposes of the figures and tables units were back transformed from $\log_{(10)}$. Differences were considered significant if $p < 0.05$. If significant main effects or interactions were found, post hoc multiple mean comparisons were evaluated using Tukey's procedure.

Results

Species differences were found in the SOC percent of the population and sample. Loblolly pine ecosystems were found to have a significant higher SOC content than slash pine ecosystems for population and sample (44%,130%) respectively (Table 2). However, pH and litter were similar for both population and sample.

Objective 1. Sonication Method Evaluation

Aggregate count was completed under a dissecting microscope (Fig. 2-1). The number of aggregates per gram of soil increased with decreasing aggregate size. The 2000 to 250 µm soil size fraction was dispersed by 100 j mL^{-1}; while the two smaller size fractions required more than 200 j mL^{-1} for complete dispersion; however, at about 150 j mL^{-1} the curve began to asymptote revealing stabilization. This study shows that aggregates were dispersed by ultrasonic energy. Observations of aggregates aided by microscopy were consistent with mycorrhizal hypha and fine roots being incorporated into aggregates. Other materials among the aggregates were fecal pellets, root epidermis and insect carcasses.

Objective 2. Contrasting Aggregation in Loblolly and Slash Pine Ecosystems

ANCOVA for the variable, AOC (g g^{-1} soil), revealed that the covariate explained a significant amount of the variability ($p<0.001$), while the main effect, pine species (categorical variable), was significant ($p<0.001$). The dispersion energy was significant when used either as a continuous or categorical variable ($p<0.001$) (Fig. 2-2a, Table2-2). On average over all energy levels, loblolly pine AOC was 50% higher than that under slash pine. At the highest dispersion energy, loblolly, on average had 41% higher AOC (Fig. 2-2a, Table 2-3).

ANCOVA for the variable %AOC as % of SOC suggests that the covariate explained a significant amount of the variability ($p <0.001$); while the main effect, species (categorical variable), was significantly different ($p < 0.001$), and the dispersion energy was also significant when used either as a continuous or categorical variable ($p<0.001$). In this case slash ecosystems revealed a significant 4.1% AOC increase, with an average AOC of 20.5 % (1.6 std. error) for slash and 16.4% (1.2 std. error) for loblolly. Initial water stable aggregates were equal for both ecosystems (Fig. 2-2b, Table 2-3).

Discussion

Objective 1. Sonication Method Evaluation

Aggregate dispersion curves have only recently been used to describe qualitatively and quantitatively the amount of AOC in a soil. Microscopic evidence verified that sonication was dispersing soil aggregates, therefore the method was deemed useful for the purpose for which it was employed. The reason for higher aggregate stability in the 150-250μm, and the higher dispersion energy required for total aggregate dispersion, needs to be explored both for mechanism of stability and potential for C sequestration.

Objective 2. Contrasting Aggregation in Loblolly and Slash Pine Ecosystems

Our findings suggest that AOC in g g^{-1} soil was clearly greater in sandy surface horizons under loblolly than under slash pine ecosystems. This result could be related to the fact that there was approximately 30% more SOC reported in loblolly pine ecosystems when compared to the SOC in slash pine ecosystems (Table 2-2). One plausible explanation for this difference in SOC is that there is greater organic C addition from fine roots and leaf litter under loblolly.

Previous studies support a possible explanation about difference in SOC added to loblolly vs. slash ecosystems. A number of studies have indicated that loblolly pine produce more leaf area (Colbert et al., 1990; Jokela and Martin, 2000; Will et al., 2001; Xiao et al., 2002; Burkes et al., 2003), more fine roots (Burkes et al., 2003; Nowak and Friend, 2006) and a larger forest floor (Polglase et al., 1992) than does slash pine, particularly in plantation environments. Since SOC is a function of rate of input versus rate of mineralization, loblolly clearly inputs more organic C into the soil. Even under equal rates of mineralization, this suggests that loblolly should have higher SOC levels as long a mineralization rate under loblolly are not less than slash pine.

Our observations of aggregation on surface sandy horizons of Spodosols in North Florida revealed that soil aggregates were bound by mycorrhizal hyphae, fine roots, and microbial and fungal debris. These observations are consistent with those of Kay (1997) and Degens et al. (1996) in sandy soils. These observations combined with higher fine-root biomass and total SOC under loblolly pine plantations are sufficient to explain the increased AOC under loblolly. This knowledge enables managers to use the species that fit their needs whether it is to have more SOC added to the soil, or more crown cover for habitat management.

The slight increase of the %AOC under slash pine plantations compared to loblolly (4.1% increase on average) indicated that slash pine systems may have a slight advantage over loblolly systems in aggregating soil C. We were unable to infer the reasons for this difference; however, more importantly, data indicated that greater than 40% of total SOC was incorporated into soil aggregates under both slash and loblolly pine ecosystems. Sarkhot et al. (2007a) also found that approximately 45% of total SOC was incorporated in aggregates. These results suggest that if AOC is physically protected in sandy soils of north Florida, then promoting loblolly pine and soil aggregation could be potentially important management objectives for increasing soil C sequestration in these soils.

Due to their dominance in Florida ecosystems, pine ecosystems play an important role in the conversion of atmospheric CO_2 into the SOM pool to sequester SOC. Loblolly pine ecosystems in north central Florida have 30% more SOC than slash pine ecosystems. This species benefit translates into a C increase that would be equal to an increase of about three million dollars of CO_2 in C credits for north central Florida; based a price of twelve dollars per ton of CO_2 (Clear Sky Solutions, 2008). Clearly the selection of loblolly over slash pine on flatwood soils affects more than just forest productivity.

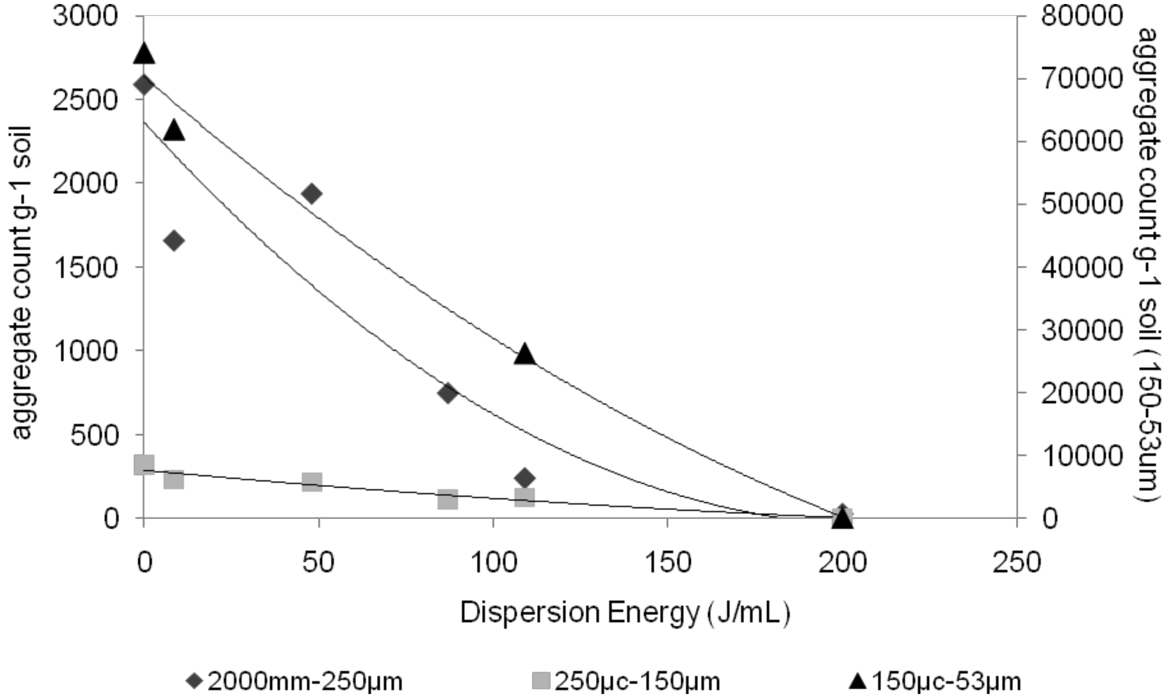


Figure 2-1. Number of aggregates per gram of soil as affected by level of dispersion energy applied and by the soil size fraction.

2a

2b

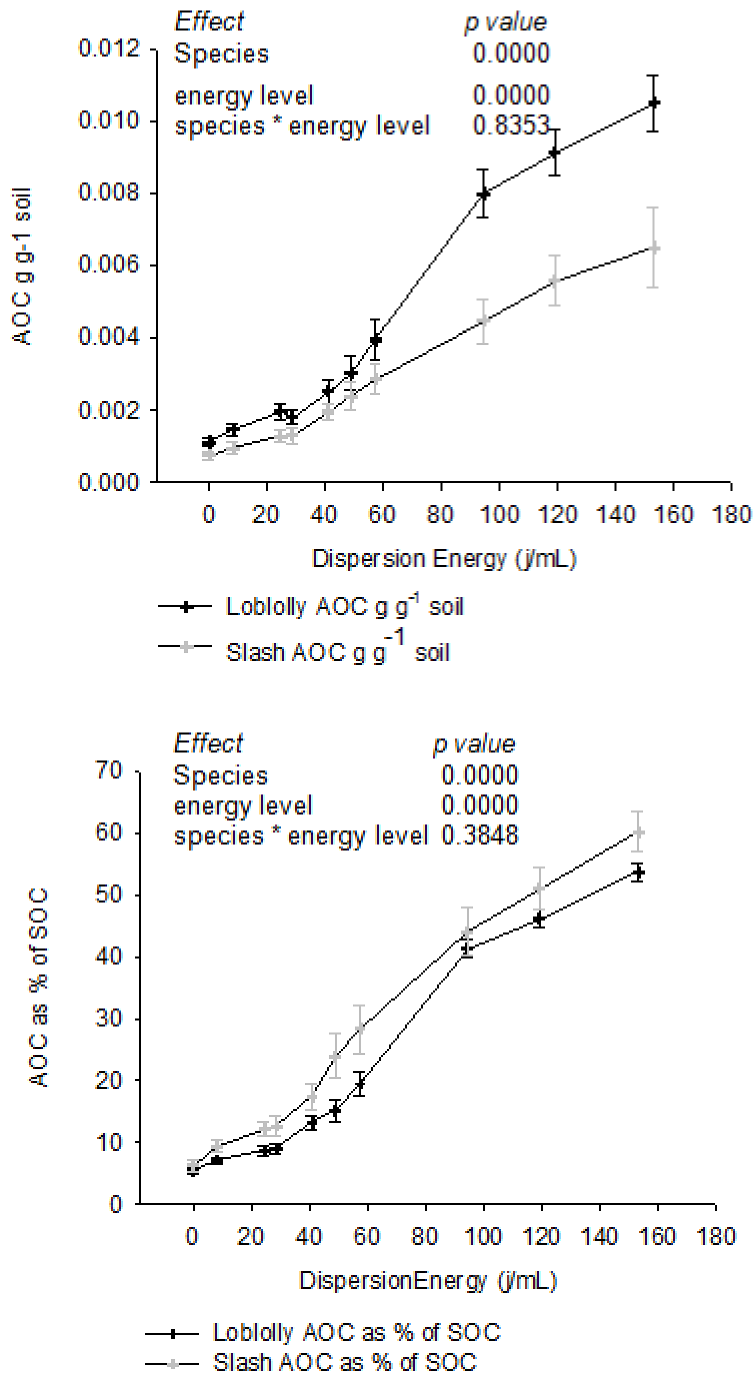


Figure 2-2. Aggregate organic carbon (AOC) as a function of dispersive energy applied to the soil when expressed as a) %AOC (% of Soil Organic Carbon) by species and b) AOC (g g^{-1}) soil by species.

Table 2-1. Sample characterization of pine sites located in North Central Florida.

County	*Dominant Species*	*Latitude*	*Longitude*	*Taxonomic class*
Alachua	L	29.711580	-82.343671	hyperthermic Ultic Alaquods
Duval	L	30.465195	-81.530360	thermic typic Alaquods
Lafayette	L	30.017988	-83.302321	thermic Aeric Alaquods
St. Johns	L	29.858920	-81.361572	hyperthermic Ultic Haplaquods
Taylor	L	29.866656	-83.418372	thermic Alfic Alaquods
Taylor	L	29.836545	-83.428403	thermic Spodic Psammaquents
Flagler	L	29.486148	-81.317456	hyperthermic Aeric Alaquods
Clay	S	30.159932	-81.945865	thermic Ultic Alaquods
Clay	S	29.891132	-81.853681	thermic Aeric Alaquods
Lafayette	S	30.017128	-83.154864	thermic Ultic Alaquods
St. Johns	S	30.088603	-81.534517	hyperthermic Typic Alaquods
Clay	S	29.849814	-81.663151	thermic Aeric Alaquods
Volusia	S	29.206476	-81.512600	hyperthermic Aeric Alaquods

Table 2-2. Characterization of population and sample, significant differences ($p<0.05$) by species.

Species	Soil Organic Carbon %	pH	Forest Floor (Kg m^2)
	Population Means (Std. Error)		
Loblolly	1.72 (0.2) **	3.53 (0.09)	1.52 (0.49)
Slash	1.20 (0.09) *	3.68 (0.06)	1.92 (0.45)
	Sample Means (Std. Error)		
Loblolly	2.36 (0.26)**	3.48 (0.17)	4.07 (1.55)
Slash	1.02 (0.15)*	3.44 (0.10)	2.23 (0.35)

* Significantly lower means

** Significantly higher means

Table 2-3. Summary of aggregate organic carbon (AOC) as influenced by tree species. Statistical differences are outlined * for lower and ** for higher means.

Species summary				
	Slash		Loblolly	
	Mean	std. error	Mean	std. error
AOC (g g^{-1} soil)	0.0065 *	0.0011	0.011**	0.0008
AOC (% of Soil Organic Carbon)	60 **	3	53 *	1
Highest dispersion level				
AOC (g g-1 soil)	0.0022 *	0.0002	0.0033 **	0.0003
AOC (% of Soil Organic Carbon)	20.5097**	1.6502	16.4116 *	1.2633

CHAPTER 3

DOES AGGREGATION PROTECT C IN VERY SANDY SURFACE SOILS?

The two major biological fluxes of C dioxide in nature are photosynthetic fixation and global respiration. They cycle about 7% of atmospheric C annually. Moreover, 15 years of photosynthetic fixation, without renewal by respiration, would cause the exhaustion of the C dioxide in the atmosphere (Sylvia et al, 2005). The large pool of global soil C is susceptible to anthropological changes that occur with land use that can result in positive or negative changes. Further understanding of how C is stored in soils is necessary in order to determine the possible management strategies that maintain soils as a major C sink. These strategies should be a function of soil characteristics.

Soil is a C sink when it can protect the SOC from decomposition and when C input occurs at a rate faster than C release. It is thought that SOC is protected within aggregates physically, chemically and physiochemically (Golchin et al., 1994; Blanco-Canqui and Lal, 2004). Soil organic C turnover rates have been found to decrease from macro- to microaggregates, therefore suggesting an increasing protection of SOC by microaggregates (Besnard et al., 1996); an idea supported by Franzluebbers and Arshad (1997) as well as by Sainju et al. (2003). It has been revealed that C storage provided by macroaggregates is greater in quantity but transient in terms of physical protection (Tisdall and Oades, 1982). Wild (1988) documented that the quality of the SOC in microaggregates is biochemically recalcitrant with low turnover rates.

Physical protection by aggregates is the incorporation of SOM within macro and microaggregates (Tisdall and Oades, 1982; Golchin et al., 1994; Jastrow, 1996); yet the ability of soils to protect C through aggregation is also dependent on soil texture and time. SOC residence times in macro- and microaggregates differ depending on the physiochemical attraction between mineral and organic particles, and the location of the organic material within the aggregate (Emerson, 1959). Buyanovsky et al. (1994) worked with agricultural soils in a 4 yr decomposition study and found that turnover rates were 1-3 yrs for macroaggregates and about 7 yrs for microaggregates. On the other hand, Skjemstad et al (1990) found no remarkable difference between the macro and micro-aggregates of an Australian sandy soil. Christensen (1987), working with loamy sand and sandy loam soils, found no physical protection by aggregation.

Sandy soils make up a soil subgroup that, while having been studied for micro and macroagregation, (Sarkhot, 2007a,b; Tisdall and Oades, 1982; North, 1976; Christensen, 1992; Cambardella and Elliot, 1993; Six et al., 2001; Swanston et al., 2005), have not been well evaluated as to its ability to protect C through aggregation (Sarkhot et al., 2007a).

As with aggregation in general, the amount of DOC contained in aggregates and the mineralizability of the DOC in aggregates has been poorly understood, particularly for sandy soils. Dissolved organic matter is a controlling factor in soil formation. DOC in forest floors have been hypothesized to be generated from leaching and microbial decay of humus (McDowell and Likens, 1988). Fluxes of DOC from the forest floor that leaches into the mineral soil were estimated to represent 35% of the annual litterfall (Guggenberger and Zech, 1993; Currie et al., 1996; Michalzik and Matzner, 1999; Solinger et al., 2001). Previous incubations showed 5-93% of DOM in soil solutions to be potentially microbially degradable (Kalbitz and Kaiser, 2008; Jandl, 1999; Kalbitz et al., 2000; Sachse et al., 2001; Kalbitz et al., 2003; Don and Kalbitz, 2005; Kiikkil et al., 2006). Dissolved organic matter with large amounts of C was found to be rich in aromatic functional groups and poor in carbohydrates (Qualls and Haines, 1992; Jandl and Sollins, 1997; Jandl and Sletten, 1999; Volk et al. 1997; Kalbitz et al., 2003; Kiikkilä et al., 2006). As a result, a large amount of dissolved organic matter that percolates to the mineral soil appears to be stable (Fröberg et al., 2006); supporting the DOC mineralizability numbers on the lower end of the range. However, if DOC is a stable source of C then if it is within aggregates it could be another pool of protected C.

The strength with which aggregates are held together describes their ability to withstand disturbance. Aggregate dispersive energy (ADE) has been used to characterize aggregate strength in a variety of soils (North, 1976; Christensen, 1992; Cambardella and Elliot, 1993; Six et al., 2001; Swanston et al., 2005). One would assume that ADE would play a role in protection of soil aggregate C; however, the relationship between ADE and C mineralization within aggregates has not been studied.

The overall objective of this study was to evaluate the role that aggregation plays in SOC protection in the very sandy soils of the Lower Coastal Plain found under loblolly and slash pine ecosystems. This was achieved by addressing 2 aims. The first aim was to determine if ADE and ecosystem cover type (slash vs. loblolly) were controlling factors in SOC and AOC accumulation and mineralization. The central hypothesis was that ADE expressed more control than species because the strength of aggregates would inhibit the release of AOC, while minimizing the entry of decomposing microorganisms. This conclusion was drawn from aggregation theories that proposed that encrustation of SOM in microaggregates is the principal pathway of C sequestration.

The second aim was to Identify SOC chemical characteristics that could explain differences at AOC stability levels and SOC chemical characteristics that could explain differences in SOC mineralization between ecosystems cover types. We hypothesized above that in North Florida's sandy soils; the mineralizability of AOC would be a function of the ADE but not of ecosystem cover type. We hypothesized here that the chemical fingerprint of SOM via DRIFTS would back up those suppositions by showing differences in the SOC fingerprints where mineralization differences were identified. loblolly or slash pine ecosystems.

Methodology

Experimental Sites and Field Sampling

The experimental sites were chosen from a previous stratified random sampling plan for a large scale research project with the objective of developing a soil C inventory of the state of Florida (Myers, unpublished data), designed to proportionally sample sites relative to the land use pattern. The study area used for this research was NRCS Conservation Area 2 located in North Florida. From this set of 55 sampling locations, 13 sites were selected. Seven sites supported a loblolly pine (*Pinus taeda* L.) ecosystem and 6 sites supported slash pine (*Pinus elliottii* Engelm.) ecosystems. Originally 7 slash pine sites were chosen but during the study it was discovered that one site had been misclassified and was discarded. The sites were chosen so that they represented the mean and the range of soil C reported in the larger data set. Soil samples in the surface 20 cm were collected at the sampling locations with 4 cylindrical cores of 30 x 5.8 cm. The forest floor was sampled at the same sites with a 23 cm^2 litter sampler. Sampling sites were located in the north Florida counties of Alachua, Citrus, Clay, Duval, Flagler, Lafayette, St. Johns, Putnam, Taylor, and Volusia (Table 1). Most study sites were

Spodosols (Aquods) (Table 3-1). The climate of the region was hot and humid with an average yearly precipitation of 113.3 cm, and yearly average minimum and maximum temperatures of 14°C and 27°C, respectively (Southeast Regional Climate Center, 2010).

The sampling sites were located on Flatwood landscapes; which are predominantly somewhat poorly to poorly-drained soils with a seasonally high water table. Loblolly and slash ecosystems had a common understory of saw palmetto (S. s*erenoa repens Small*), wax myrtle (*myrica cerifera* L), gallberry (*ilex glabra* L.), brakenfern (*pteridium aquilinum* L.), blackberry (*rubus sp*.), and fetterbush (*Lyonia lucida* Lam.). Various grasses were common, such as bluestem (*Andropogon virginicus* L.) and wiregrass (*Aristida beyrichiana*). Perennial woody species included young oaks (*Quercus sp*.) like water oak (*Quercus nigra* L.), sweetgum (*Liquidambar styraciflua* L.), bays (*Persea sp*.), and Florida maple (*acer barbatum*). Both loblolly and slash in ages ranged from 10-20 years. All but one of each species was in a plantation setting. However, one loblolly and one slash pine site were natural pinelands.

Laboratory Methods

Soil Samples obtained from the field were measured for moisture content, and then air-dried in a greenhouse before passing through a 2mm sieve. Bulk density was calculated by a core method (McIntyre, 1974). Soil pH was measured by the protocol of Thomas (1996). A comparison of the 13 sites used in this study to the total sites available for sampling from the larger study show that these study sites are representative (Table 3-2).

One-hundred grams of air-dried and sieved samples were dry sieved through a 53 microns sieve for 5 min at 75 rpm using a horizontal mechanical shaker (Sarkhot et al., 2007a). Samples used in analyses were all larger than 53 µm and smaller than 2000 µm (2mm), this would include macro and microaggregates.

Mineralization

An incubation study was utilized to determine if the ADEC was a controlling factor in AOC mineralization/protection. To that end microcosm for each soil sample were constructed, where each microcosm contained 20 grams of soil, 0.05 grams of soil inoculum and a liquid base trap of 20 mL of 0.25 M NaOH. The soil inoculum was added to provide a microbial population that could have been eliminated due to the sonic energy application. Each site used in this study was represented by nine microcosms that reflected three replications of three treatments. The treatments were no energy applied, energy applied at mid-range of the ADE curves (ADEC), and energy applied at the higher level of the ADEC (0, 140, and 260 j mL^{-1} respectively).

Since the sonication process required soil saturation, subsequent to the application the ADE each sample was filtered through a vacuum system at a pressure of 0.33 bars using a 22µm membrane (Schwesig et al., 2003).Each soil sample (20 g) were placed in a microcosm to begin the incubation study. The 0.22 µm membrane was used to minimize the amount of DOC removed from the soil. The DOC was measured with a Shimadzu TOC-VCPH Analyzer (Shimadzu Scientific, Columbia, MD.).

The microcosms were placed in an incubator at 35°C. The water content was maintained by weight, and the base traps were changed periodically at weeks 4, 7, 12, 15, 19, 21, 25, and 29. When base traps were changed each sample was opened and its atmosphere was replaced by ambient air. The soil respiration, or alkaline trap method, was utilized to determine the rate of C dioxide (CO_2) evolution (Anderson, 1982). In this method the trap functioned as a sink for evolved CO_2 from the soil. The 0.25 M NaOH base solution was titrated with 0.1 M hydrochloric acid (HCl).

The following formula was utilized to measure C (mg) from respired $C0_2$ measured through titration from the SOC and DOC (see below) incubation studies:

C (mg) respired = [(B-T) x M x E]/ DF

Where B is the mL needed to titrate blank aliquot. T is the volume in mL needed to titrate the sample aliquot. M is the normality of the acid, in this case HCl. E is the equivalent weight, in this case the equivalent weight of C (E=6) was utilized. DF is the dilution factor of the base trap (Anderson, 1982).

Dissolved organic carbon (DOC)

In order to determine the mineralization rates of the DOC solutions, a mineralization study was initiated where 60 mL of soil solution were poured into a 250 mL Erlenmeyer flask which had 0.05 g of soil inoculum. The average of C in 60 mL was 0.54 mg with a standard error of 0.26. The CO_2 evolved was measured as detailed above. All microcosms were sealed and placed in a dark incubator at 35° C for 84 days. Samples were periodically shaken manually. Due to the small portion that DOC represents of the TOC, and due to the lack of differences between species and dispersion level, the mean DOC mineralization rate was used to calculate DOC mineralized over time and this was added to the mineralization of SOC to provide the total C mineralized from the TOC.

Fourier transformed infra-red reflectance (FTIR) spectroscopy

Fourier transform infrared spectroscopy's utility is based on its sensitivity, spectral precision, reproducibility and fast spectral acquisition time (Johnston et al., 1996). This method was utilized to describe organic C chemistry present by: species, incubation periods and dispersion energy levels. The chemical composition of species, dispersion levels, and mineralization progression was investigated using DRIFTS in the mid-IR (4000-400cm^{-1} or 2500-25000 nm). Spectra were run on a DigiLab FTS-7000 FTIR instrument (Varian, Inc., Walnut Creek, CA). Samples were placed in a Pike AutoDiff 60-cup auto sampler (PIKE Technologies, Madison, WI) (Reeves, personal communication). Ground samples were placed in the auto sampler cups and scanned using a KBr beam splitter and deuterated triglycine sulfate (DTGS) detector. Spectral subtraction of ashed samples from un-ashed samples was utilized to emphasize the organic composition; this subtraction was completed utilizing GRAMS/AI software, Version 7.02 (Thermo Galactic, Salem, NH) (Sarkhot et al., 2007a). Spectrum by species were averaged from the ash-subtracted spectra from each site, and a discriminant analysis was performed to quantify how different was the separation between ash-subtracted species, mineralization days, and dispersion energy levels. Discriminant analysis was completed using a modified SAS program adapted to examine spectra (Reeves and Delwiche, 2008, Sarkhot et al., 2007a).

Statistical Analysis

Two separate analyses were run, one for the SOC incubation study and another for the combination of the SOC and DOC called TOC. The results of the statistical analyses for both differ only in the last three time periods of the incubation study. These results suggest that DOC can be an influential fraction of the TOC turnover especially towards the end of the incubation study, since the addition of the DOC rate influenced the results from having species that were significantly different (without DOC addition) to statistically insignificant species. The statistical results presented here were for the analysis of the TOC mineralization. The soil and DOC mineralization rates were combined to define TOC mineralization and a GLM repeated measures analysis was ran in STATISTICA (Statsoft, Inc. 9.0; Tulsa OK). The main effects were Species and Energy Level. Differences were considered significant if $p < 0.05$. If significant main effects or interactions were found, Tukey's post hoc multiple mean comparisons procedure was utilized.

An ANCOVA was applied to the total DOC data and the DOC released at the three sonication energy levels. The covariate in these analyses was TOC (mg g^{-1} soil), while the main effects were Energy Level and Species (Table 3-3). Differences were considered significant if $p < 0.05$. If significant main effects or interactions were found, Tukey's post hoc multiple mean comparisons procedure was utilized. For the purposes of figures and tables all $\log_{(10)}$ means resulting from statistical analyses were back transformed.

Results

Objective 1. Determine if Aggregate Stability Levels and Ecosystem Cover Types were a Controlling Factor in SOC and AOC Accumulation and Mineralization.

Our results revealed that the ADE level of soil aggregates was not a factor in protecting AOC (Fig. 3-2). Even though periodic specific mineralization rates of TOC under slash pine was not statistically different from loblolly pine, the cumulative effect over time was significant resulting in higher specific C mineralization rates in slash pine influenced soils; approximately 8% higher than found in soils influenced by loblolly pine (Fig. 3-1a).

Loblolly pine soils released more DOC from the aggregates than did slash pine soils as ADE increased (Table 3, Fig. 3-3). At the highest ADE, loblolly pine soil released an average of 36% more DOC in mg g^{-1} soil than did slash pine soils. This is attributed to the fact that loblolly pine soils had higher amount of TOC. Dissolved Organic C incubation results revealed that by day 84 there was no significant effect of the dispersion energy or species on DOC mineralization rate (Table 3-3).

Objective 2. Identify SOC Chemical Characteristics that could explain Differences at AOC Stability Levels and Mineralization between Ecosystems Cover Types.

Discriminate analysis produced a poor separation of ash-subtracted dispersion energy levels as evidenced by R^2s of 0.07, 0.00, and 0.05, respectively (Table 3-5). However, DRIFTS analysis identified distinctly different spectra for slash pine and loblolly pine influenced soils. Spectral bands between 2000 and 1200 cm^{-1} in the non-ashed samples (Fig. C-1, C-2) are related to silica, revealing soils with high mineral matter (Reeves III and Smith, 2009). Yet, comparison of the average of ash-subtracted spectra for both species supported the higher organic matter in loblolly soils (Figure 4), and indicated that the functional group assemblages were also influenced by ecosystems. Figure 5 represents the difference of ash-subtracted loblolly minus slash averaged spectra. Slash appeared to have more aliphatic C-H indicated by the bands between 2900-3000 cm^{-1} (Reeves III and Smith, 2009; Madari et al., 2005). Loblolly appeared to have more aromatic carboxylic acids as indicated by the bands around 1600-1700 cm^{-1} (Reeves III et al., 2006; Celi et al., 1997).

Discriminant analysis for ash subtracted (R^2 = 0.875, SE = 0.176) and for non-ash subtracted spectra (R^2 =0.977, SE = 0.176) showed that ash-subtracted spectra provided a stronger contrast; indicating that organic compounds were responsible for the differences seen between species, rather than mineralogy (Table 3-4). Therefore, ash-subtracted spectra were used for subsequent analyses.

Ash-subtracted spectra for week 29 and week 1 from the incubation study provided a distinct difference. Discriminant analysis produced a high R^2 (Table 3-6) and indicated that mineralization had affected each species differently. Figure 3-6 shows loblolly pine ecosystems experienced a large decrease in reflectance in the wave number range of 3000 to 3600 cm^{-1}. This is a general region for OH and typical for humic acids. The triplet band at 1800 to 2000 cm^{-1} is due to an increase in silica over time as OM decreases. Finally, an accumulation of aromatics occurs with the degradation of the humic substances. Alternatively, the subtraction spectra between week 29 and week 1 for slash pine ecosystems also appeared to have an increase in C-H aliphatic carbon, indicated by the bands around 2900-3000 cm^{-1}. Figure 3-7 reveals large peaks at 3000-3500 cm^{-1} (peaks 3531, 3460, 3170, and 3054) and a specific peak at 1295 cm^{-1} which are attributed to aliphatic materials. The triplet band at 1800 to 2000 cm^{-1} is due to an increase in silica over time as OM decreases. Overall, there is an accumulation of aliphatic materials in slash pine over time; on the other hand, loblolly shows an accumulation of humic materials and aromatic material over time as other OC degrades.

Discussion

Our initial hypothesis was that ADE would be a controlling factor in the accumulation and protection/sequestration of AOC; while ecosystem cover type would not be a factor. Our results from the TOC incubation study suggest no effects of aggregate dispersive energy on turnover rates, and an effect between ecosystem cover types; rejecting our hypothesis (Fig. 3-2).

Total organic C mineralization rates were a product of the combination the DOC and SOC separate incubations. In sandy soils under pine ecosystems of slash and loblolly pine there was no significant difference in the TOC mineralization rates of aggregates at different stability levels. Findings support the contention held by some that SOC mineralization is more related to the stability/liability of the SOC than to the physical protection of aggregation (Christensen, 1985, 1987; Buyanovsky et al.1994). Our results conflict with the concept that the formation of macroaggregates facilitates the accumulation of organic matter, and given favorable conditions physical protection is promoted (Jastrow, 1996). The reason why our results conflict with this concept may be that favorable conditions are not promoted in Florida's soils with characteristics like: <10 $cmol_c\ kg^{-1}$ cation exchange capacity, and less than 5% silt plus clay (Carlisle et al., 1981,1988, 1989).

While we did not expect species to have a control on mineralization; the SOC under the two different ecosystem cover types did mineralize differently (Fig. 3-1). The soil under slash pine had higher specific mineralization rates, even though the total mineralization under loblolly pine was greater - due to a significantly larger SOC content under that species (Table 3-2). This is the first time that SOC mineralization from soils influenced by these two ecosystems has been contrasted; both in terms of mineralizability and DRIFTS spectra for chemical differences. The lower mineralization rates, combined with the higher organic matter inputs under loblolly pine explain the higher SOC levels found in the previous chapter.

Mid-infrared spectroscopy has been found capable to predict soil properties like organic and total C (Minasny et al., 2009). Mid-infrared spectra were utilized to analyze relationships throughout the incubation study. This method identified chemical differences in the samples from the incubation study between: dispersion energy levels, pine ecosystems and incubation periods. Results revealed no irrefutable difference between dispersion energy levels or stability levels measured in the incubation study. On the other hand, definite differences were found in respect to species chemical composition. Spectra comparisons between the two soils under different ecosystems reflect the greatest distinction between ecosystems (Fig. 3-3, 3-4). More aliphatic C-H present in slash could be related to waxes or methyl groups which are more bioavailable than the larger amount of aromatic carboxylics present in loblolly pine ecosystems. Differences found comparing incubation times were also evident only for week 1 and week 29 (last week of the incubation). The last week of the experiment revealed a change in the patterns of the chemical composition: a decrease in humic acids and increase in aromatics of loblolly, and an increase in the aliphatic C-H of slash over time (Fig. 3-5, 3-6).

Another significant finding was related to the DOC incubation study, in that it was identified as an important component of TOC turnover. Our findings are congruent with Zhao and Kalbitz (2008); who did a study in China in forested Typ-Ishumisol soils sampled to a depth of 20 cm and revealed an average mineralization of 0.06 g kg^{-1} day^{-1} of DOC, which was similar to our findings of 0.05 g $kg^{-1}day^{-1}$ of DOC mineralization rate. Schwesig et al (2003) studied DOC mineralization released by water extractable C coming from the surface 20 cm of spodosols dominated by Norway spruce (*Picea abies*); however, they found a total mineralization rate over 97 days of 0.0004g kg^{-1}. Our results are similar to Zhao's measurements and our findings suggest that DOC is an important component of aggregation in surface spodosols; the evidence is shown in Figure 2 where as increasing ultrasonic energy is applied there is an increasing release of DOC.

In the end, our findings warranted rejection of our hypothesis. No differences were revealed between energy dispersion levels, a finding supported by both incubation and mid-IR analyses. However, findings suggest a significant difference in the C quality between species. The quality of needles and roots of loblolly vs. slash has not been widely studied and these data imply that more detailed work on the quality of organic matter inputs (roots, leaves, branches) will be necessary in order to quantify C cycling between these species. Comparisons between cover types are important in order to understand how SOC is related to the forest floor material and, ultimately, its influence in soils as a sink of C.

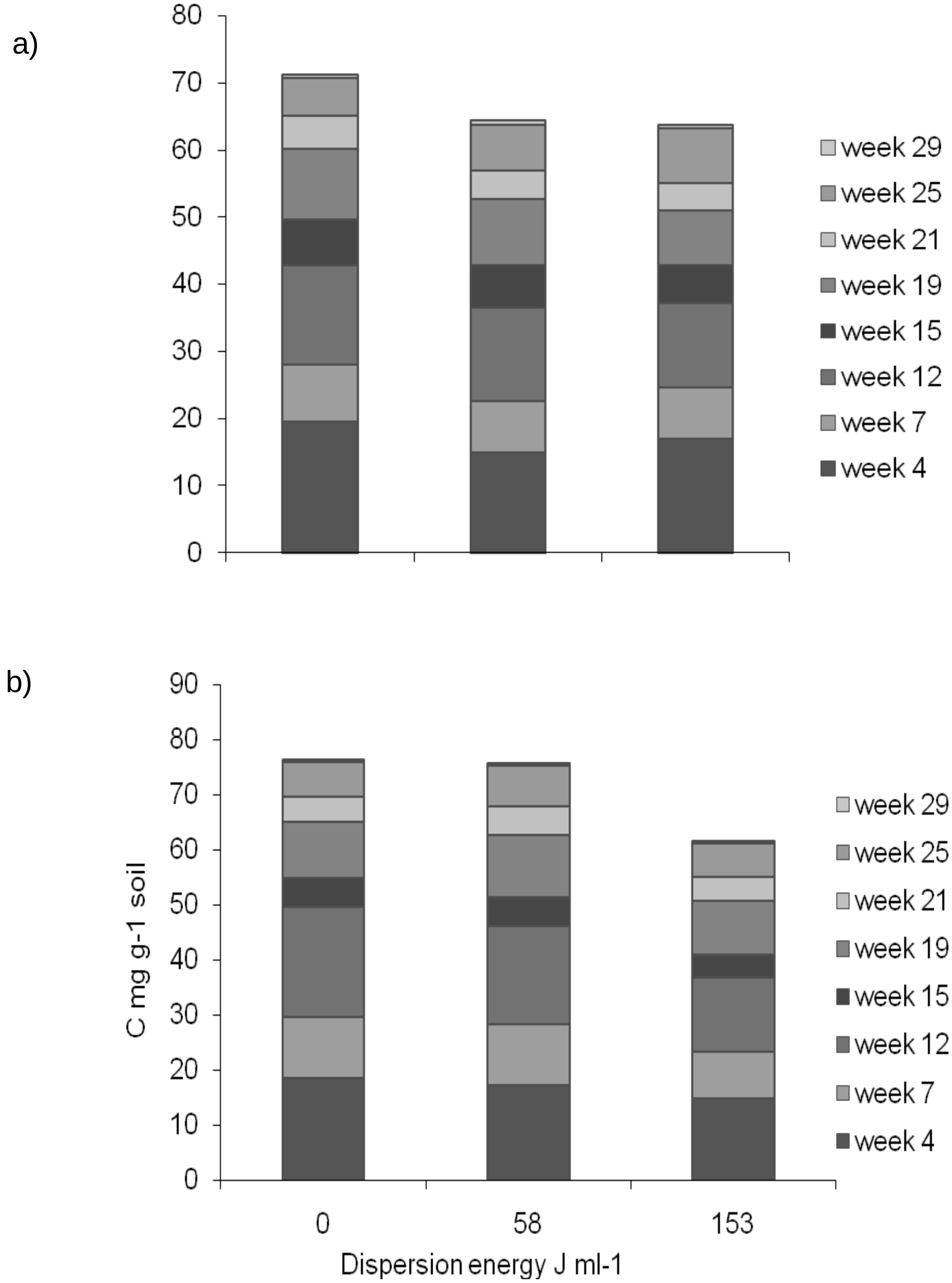


Figure 3-1. Comparison of the carbon (C) mg g^{-1} soil by dispersion energy levels (J mL^{-1}) by week for: a) loblolly and b) slash pine ecosystems. There were no significant differences found between the ADE levels for each period.

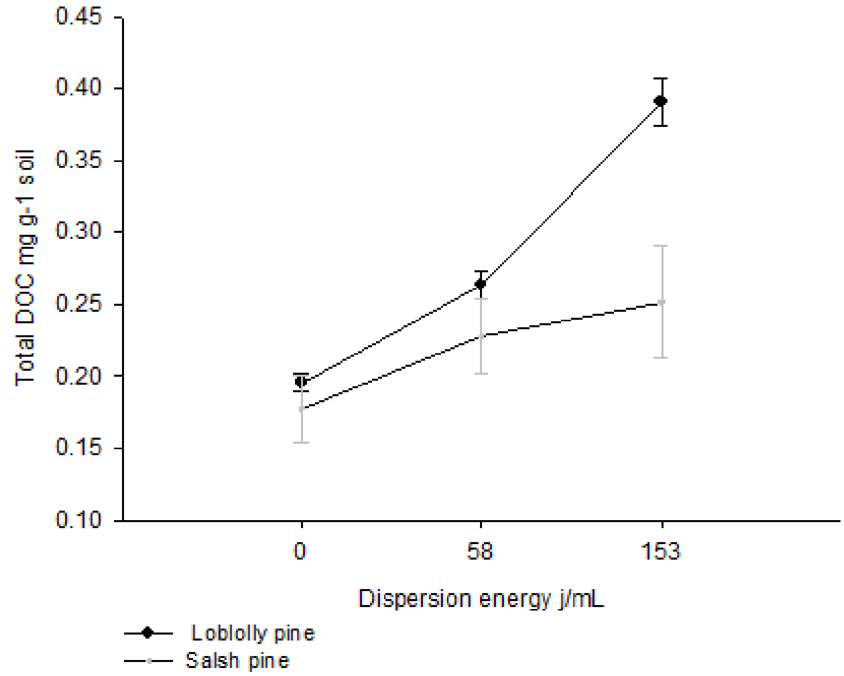


Figure 3-2. Total dissolved organic carbon (DOC) dispersed from the soil when three dispersion energy levels were applied via sonication. Significant differences are illustrated at dispersion energy of 153 j mL^{-1}.

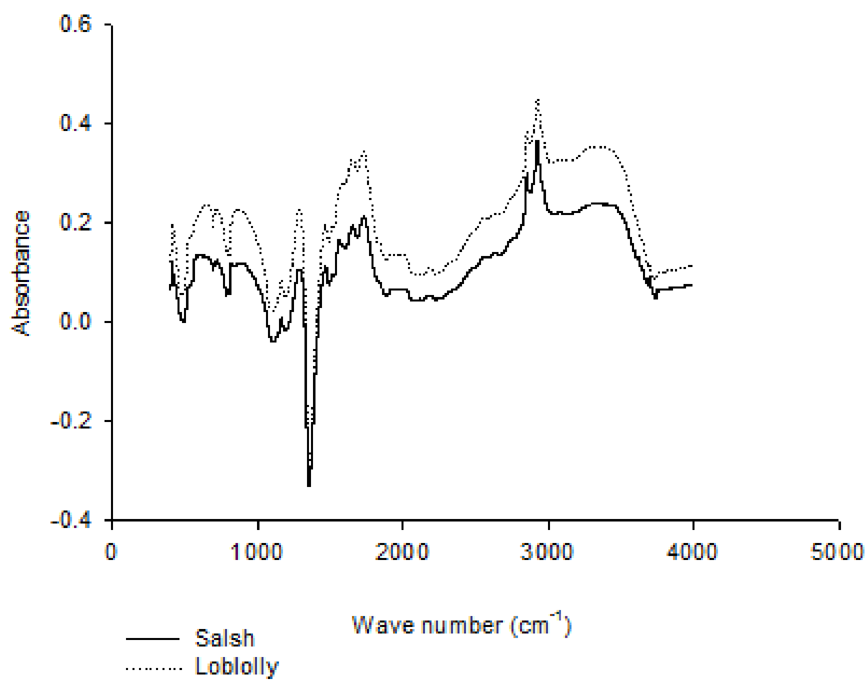


Figure 3-3.Diffuse reflectance infrared Fourier-transform spectra fingerprint of the average ash subtracted spectra.

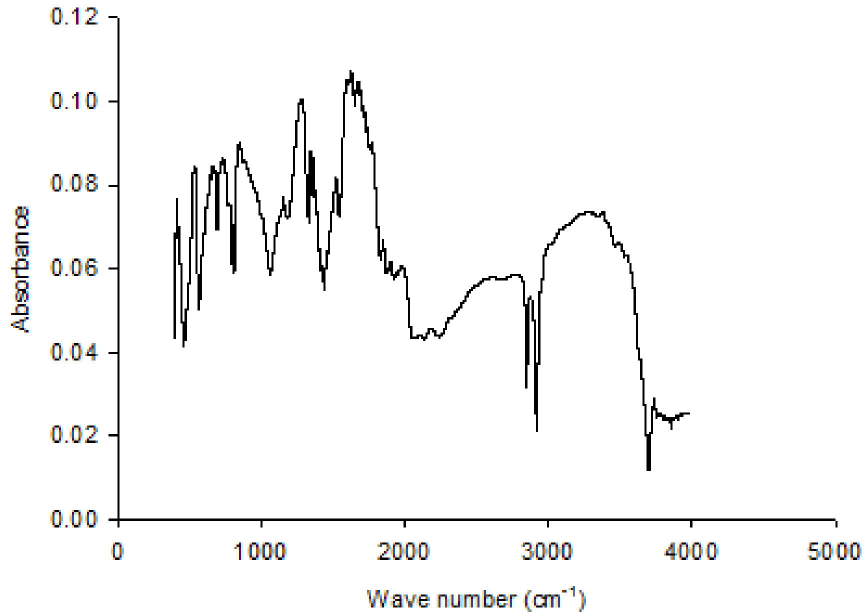


Figure 3-4. Diffuse reflectance Fourier-transform spectra of the difference between spectra of ash-subtracted loblolly minus slash pine influenced soils. In this graph it is possible to see slash pine ecosystems appear to have more aliphatic C-H indicated by the region around 2900-3000 cm-1 than loblolly pine; and loblolly pine ecosystems reveal more aromatic carboxylic acids present at wavelengths 1600-1700 cm-1.

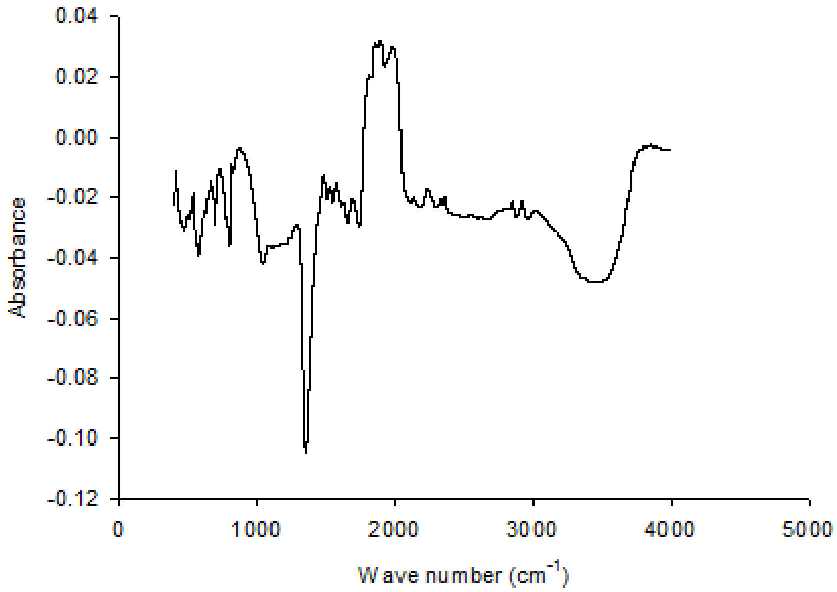


Figure 3-5. Spectral subtraction between weeks 29 and 1 for loblolly pine influenced soils. Absorbance located above 0.00 indicates an increase of week 29 over week 1 and absorbance below 0.00 indicate the opposite. This figure reveals that in the wave number range of 3000 to 3600 cm-1 in week 1 there was more OH and humic acids. The triplet band at 1800 to 2000 is an increase in silica over time as organic matter decreases

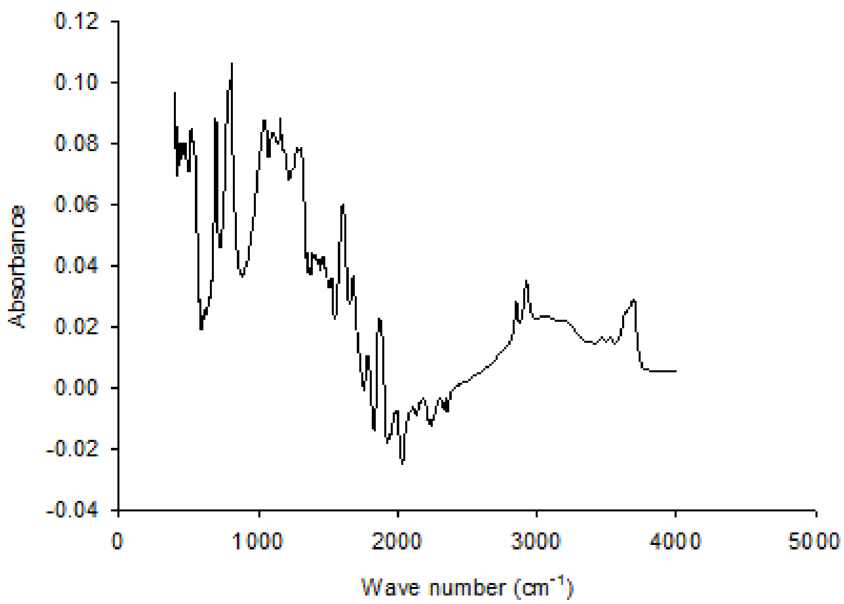


Figure 3-6. Spectral subtraction between weeks 29 and 1 for slash pine influenced soils. Absorbance located above 0.00 indicates an increase of week 29 over week 1 and absorbance below 0.00 indicate the opposite. Wave numbers between 1600 and 400 reveal over time increase in the CH, OH and aliphatic materials, and the large peaks at 3000-3500 and a specific peak at 1295 are also an increase over time attributed to aliphatic materials.

Table 3-1. Description of sample sites

County	Dominant Species	Latitude	Longitude	Taxonomic class
Alachua	L	29.71158008	-82.34367117	hyperthermic Ultic Alaquods
Duval	L	30.46519541	-81.53036099	thermic Typic Alaquods
Lafayette	L	30.01798816	-83.30232129	thermic Aeric Alaquods
St. Johns	L	29.85892000	-81.36157200	hyperthermic Ultic Alaquods
Taylor	L	29.86665683	-83.41837283	thermic Alfic Alaquods
Taylor	L	29.83654543	-83.42840383	thermic Spodic Psammaquents
Flagler	L	29.48614818	-81.31745613	hyperthermic Aeric Alaquods
Clay	S	30.15993245	-81.94586597	thermic Ultic Alaquods
Clay	S	29.89113266	-81.85368181	thermic Aeric Alaquods
Lafeyette	S	30.01712800	-83.15486400	thermic Ultic Alaquods
St. Johns	S	30.08860306	-81.53451760	hyperthermic Typic Alaquods
Clay	S	29.84981430	-81.66315102	thermic Aeric Alaquods
Volusia	S	29.20647699	-81.51260040	hyperthermic Aeric Alaquods

Table 3-2.Population and Sample means with corresponding standard errors for total carbon (TC), soil organic carbon (SOC)

Species	TC %	SOC %	pH	Forest Floor (Kg m^2)
Population Means				
loblolly	2.08 (1.05)	2.00 (1.04)	3.70 (0.74)	3.34 (3.62)
Slash	1.57 (1.06)	1.57 (1.06)	3.74 (0.42)	2.72 (2.79)
Sample Means				
loblolly	2.45 (0.68)	2.45 (0.68)	3.5 (0.45)	3.83 (2.56)
Slash	1.68 (1.51)	1.67 (1.52)	3.66 (0.57)	3.74 (3.80)

Table 3-3. Total Dissolved Organic Carbon mg g^{-1} soil with corresponding standard errors and species comparisons. Significant differences ($p<0.05$) by species are indicated by a * for lower and ** for higher means.

J mL^{-1}	Slash		Loblolly	
0	0.17748	(0.002) *	0.19561	(0.021) *
58	0.22793	(0.024) *	0.26372	(0.028) **
260	0.25140	(0.028) *	0.39023	(0.045) **

Table 3-4. Discriminant analysis for the separation of species from spectral analysis displayed by R^2 and Residual Mean Squared Deviation (RMSD).

	R^2	RMSD
ash-subtracted	0.875	0.176
non ash-subtracted	0.977	0.075

Table 3-5. Discriminant analysis for spectral separation ash-subtracted of energy level is displayed by R^2 for dispersion energy level by species

Dispersion energy	loblolly	slash
0 j mL-1	0.57	0.2
58 j mL-1	0.05	0.47
153 j mL-1	0.05	0.48

Table 3-6. Discriminant analysis for mineralization study of SOC by species with R^2 and Residual Mean Squared Deviation (RMSD).

	loblolly		slash	
week	R^2	RMSD	R^2	RMSD
1	0.8	0.09	0.85	0.08
15	0.77	0.23	0.78	0.23
21	0.69	0.23	0.7	0.22
29	0.87	0.18	0.85	0.19

CHAPTER 4
SYNTHESIS

Florida's pine lands are in decline; nevertheless they are a landuse of key importance. Although in decline, pine flatwoods comprise the most extensive Florida ecosystem covering approximately 50% of the land area (Florida Forest Stewardship, 2006). Total organic C is known as a key factor to the quality of Florida's sandy soils. Knowledge about aggregate distribution and strength are crucial to the dynamics of water and air movement through soil, which in turn affects soil quality and its productivity (Blanco-Canqui and Lal, 2004). A current issue is the capability of soil aggregates to protect C from transformation by mineralization, due to the potential of soils to protect C from evolving into CO_2 which affects directly our climate change problems.

The first gap of knowledge filled by our study was the sonication method evaluation. Our results revealed microscopic evidence that sonication successfully disperses soil aggregates. The sonication method was deemed adequate to disrupt aggregates without affecting chemical composition of the organic matter. However, in order to fully understand this method, further studies on its ability to break young particulate organic matter fractions are still necessary.

Our study outlines main differences between loblolly and slash pine ecosystems in terms of total SOC, as percent and per gram of soil. SOC% was in both cases higher in loblolly than slash pine ecosystems. Although our sample was small it still was representative of the differences seen in the population (Table 2-2). The values are not necessarily reflecting equivalent management regimes, but they represent how slash and loblolly are managed in the real-life landscape. Further understanding of the relative distribution of SOC among these two ecosystems is key, in order to understand ecosystems functions and the contributions of each species on its soil as potential C sink.

It was found that loblolly had a 40% higher AOC (g g-1 soil) than slash ecosystems. One plausible explanation for this difference is that there is greater organic C addition from fine roots and leaf litter under loblolly (Nowak and Friend, 2006; Burkes et al. 2003; Xiao et al., 2002; Will et al. 2001; Polglase et al., 1992; Colbert et al., 1990). We suggest further research where a fractionation of soil may increase sensitivity and find which aggregate sizes differ by ecosystem. Previous preliminary research has shown that size fraction 150-250 μm (Azuaje, unpublished data) contain aggregates with the highest stability levels. Knowledge about AOC size fractions within 2000 and 53 μm and their relative ability to protect C has yet to be studied.

The slight increase of the AOC, as a % of SOC, under slash pine plantations compared to loblolly (4.1% increase on average) indicates that slash pine systems have a slight advantage over loblolly systems in aggregating soil C. We were unable to infer the reasons for this difference. However, more importantly, data indicated that greater than 40% of SOC was incorporated into soil aggregates under both slash and loblolly pine ecosystems, a result supported by Sarkhot et al. (2007b).

Our findings clearly show that C in Florida's sandy soils under loblolly and slash pine ecosystem is not physically protected from mineralization. Whether the results would be different with a more specific size fraction needs to be investigated. Luckily, forest management maintains a soil that is relatively undisturbed for close to two decades. During that time C will accumulate as seen by this study. However, harvesting and subsequent reforestation will put all soil C in jeopardy of being lost given this lack of physical protection.

The chemical fingerprint provided by mid-IR analysis was crucial in understanding C quality differences for stability levels and species. There were no spectral differences found between stability levels of aggregates, supporting the lack of physical protection suggested by the incubation study. As for species, mid-IR spectra revealed significant differences in the C quality in the SOC of loblolly vs. slash pine ecosystems; also supporting the previous differences in mineralization rates found between species. Further research into the chemical differences between species should yield information that will make modeling SOC mineralization more accurate. These studies should concentration on the original components of the SOM (i.e. roots, needles, and woodstem). Their comparison with SOC may reveal information about the origin of compounds present in the soil C matrix.

DOC was identified as an important component of TOC turnover based on the evidence that as increasing ultrasonic energy is applied there is an increasing release of DOC. This component should be investigated as to whether it is a significant agent for keeping microaggregates together.

Results from previous studies suggest the importance for innovative approaches for studying aggregation in sandy soils, in order to assess the long-term effects of management practices on the soil C (Sarkhot, 2007a). Due to their dominance in Florida ecosystems, pine lands play an important role in the conversion of atmospheric CO2 into the SOM pool that sequesters SOC. Loblolly pine ecosystems in north central Florida contain approximately 13.44 metric tons of C per ha-20cm depth more than slash, which translates to four hundred million dollars in CO_2 C credits increase if slash had been loblolly pine. Agricultural activities, including forestry, are net sinks that offsets over 4% of all US GHG (green house gas) emissions. Forests can mitigate GHG by adjusting the type and intensity of agricultural production (Follett, 2010). In the case of soil science a key to the reduction of GHG is in the combination of improved soil and landuse management techniques. Information about the quality and quantity of AOC at different stability levels and size fractions can aid in the generation of C footprint baselines from which we can measure improvement of C sequestration in soils.

APPENDIX A
POPULATION CHARACTERIZATION

Table A-1. Complete dataset of 56 pine sites located in north central Florida under spodosols.

County	Species	Latitude	Longitude	TC %	SOC %	PH	Litter (Kg m^2)
Alachua	S	29.712375	-82.154249	0.719	0.719	4.15	NA
Alachua	S	29.704885	-82.311552	1.056	1.056	4.04	4.012
Alachua	S	29.7535	-82.198581	0.824	0.824	3.42	1.518
Alachua	S	29.708777	-82.327257	5.045	5.045	3.46	0.660
Baker	S	30.297969	-82.088372	2.317	2.317	3.58	0.867
Baker	S	30.302311	-82.081807	0.692	0.692	3.9	0.613
Baker	S	30.298978	-82.081279	1.476	1.476	3.71	0.418
Baker	S	30.294036	-82.066642	1.171	1.171	4.13	0.576
Baker	S	30.235531	-82.310725	0.794	0.794	3.85	0.939
Clay	S	30.159932	-81.945865	0.688	0.688	3.79	0.464
Clay	S	29.891132	-81.853681	1.185	1.185	3.54	0.990
Clay	S	29.890983	-81.858647	0.984	0.984	3.24	1.623
Duval	S	30.342972	-81.869493	2.323	2.323	3.94	6.571
Flagler	S	29.481865	-81.273662	0.830	0.830	3.73	6.083
Hamilton	S	30.527465	-82.979794	0.776	0.776	4.94	2.447
Hamilton	S	30.530920	-82.736469	1.509	1.509	3.64	0.397
Lafayette	S	30.017128	-83.154864	1.580	1.580	3.33	2.514
Lafayette	S	29.88705	-83.313558	3.373	3.373	4.17	1.273
Lafayette	S	30.062431	-83.311331	1.207	1.207	3.6	NA
Lafayette	S	30.018853	-83.279406	1.755	1.755	4.2	2.032
Nassau	S	30.65586	-81.554301	1.055	1.055	3.94	2.218
Nassau	S	30.725651	-81.997664	1.116	1.116	3.86	0.331
Nassau	S	30.699379	-81.596138	2.552	2.552	3.15	0.996
Putnam	S	29.84981	-81.663151	0.950	0.950	3.4	9.542
Putnam	S	29.645555	-81.824897	1.480	1.480	4.01	1.752
Putnam	S	29.590073	-81.932761	1.097	1.097	3.39	6.642
St. Johns	S	30.005943	-81.539609	1.155	1.155	3.57	3.223
St. Johns	S	30.088603	-81.534517	0.921	0.921	4.74	1.481
St. Johns	S	29.717134	-81.301320	1.990	1.990	3.46	1.722
Union	S	30.077723	-82.40143	1.499	1.499	3.48	1.936
Volusia	S	29.206476	-81.51260	4.708	4.708	3.16	7.473
Volusia	S	29.113007	-80.993003	1.495	1.495	3.21	10.237
Alachua	L	29.711580	-82.343671	1.272	1.272	3.73	4.145
Alachua	L	29.715106	-82.150826	3.099	3.099	3.09	3.628
Baker	L	30.304482	-82.067178	0.700	0.700	3.46	2.016
Baker	L	30.333257	-82.477562	0.889	0.889	3.6	0.811
Baker	L	30.256181	-82.088706	0.797	0.797	3.69	1.339

Table A-1. Continued

County	Species	Latitude	Longitude	TC %	SOC %	PH	Litter (Kg m^2)
Dixie	L	29.542032	-83.2539598	0.786	0.786	4.1	0.848
Duval	L	30.465195	-81.530360	3.468	3.468	3.56	8.590
Duval	L	30.134640	-81.635989	2.977	2.977	3	15.775
Flagler	L	29.486148	-81.3174561	2.360	2.360	3.07	3.673
Hamilton	L	30.401772	-82.681447	1.699	1.699	3.97	2.388
Hamilton	L	30.533555	-82.735459	2.265	2.265	3.49	0.202
Lafayette	L	30.017988	-83.302321	2.182	2.182	3.2	5.322
Marion	L	29.233783	-81.917593	0.621	0.621	3.76	0.769
Nassau	L	30.596419	-81.907466	1.513	1.513	4.18	2.048
Putnam	L	29.689604	-81.745887	4.145	4.145	3.16	0.820
St. Johns	L	29.85892	-81.361572	2.493	2.493	3.23	4.276
St. Johns	L	29.952492	-81.454457	2.958	1.404	6.29	2.225
Taylor	L	29.866656	-83.418372	2.973	2.973	3.33	3.221
Taylor	L	29.836545	-83.428403	2.401	2.401	4.4	1.449
Alachua	-	29.712529	-82.1519448	5.376	5.376	2.98	3.044
Baker	-	30.241833	-82.301556	1.212	1.212	3.57	0.251
Hamilton	-	30.493726	-82.873999	1.291	1.291	3.53	2.697
Taylor	-	30.195384	-83.8684674	1.845	1.845	5.55	1.424

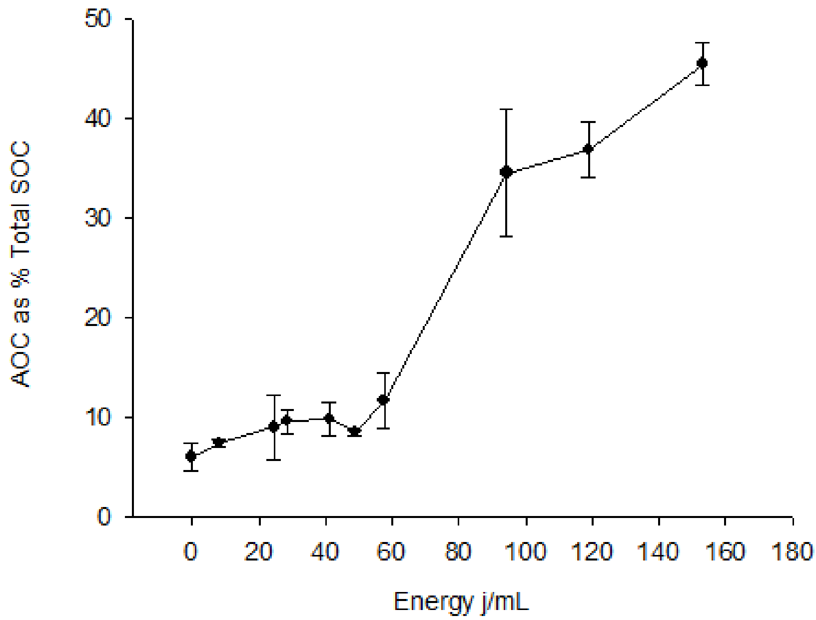
Table A-2. Slash (S) and Loblolly (L) pine ecosystem population descriptive data of Soil Organic Carbon % (SOC %), pH, and forest floor (Kg m^2).

Species	SOC %	pH	Forest Floor (Kg m^2)
S	1.495	3.21	10.237
S	4.708	3.16	7.473
S	0.830	3.73	6.083
S	1.097	3.39	6.642
S	1.480	4.01	1.752
S	1.056	4.04	4.012
S	5.045	3.46	0.660
S	0.719	4.15	NA
S	1.990	3.46	1.722
S	0.824	3.42	1.518
S	0.950	3.4	9.542
S	3.373	4.17	1.273
S	0.984	3.24	1.623
S	1.185	3.54	0.990
S	1.155	3.57	3.223
S	1.580	3.33	2.514
S	1.755	4.2	2.032
S	1.207	3.6	NA

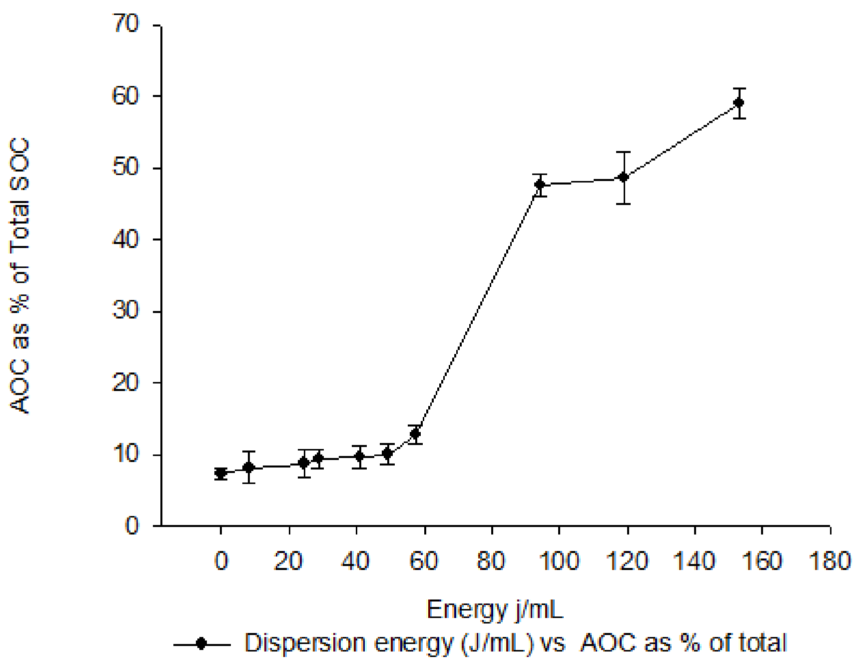
Table A-2. Continued

Species	SOC %	pH	Forest Floor (Kg m^2)
S	1.499	3.48	1.936
S	0.921	4.74	1.481
S	0.688	3.79	0.464
S	0.794	3.85	0.939
S	1.171	4.13	0.576
S	2.317	3.58	0.867
S	1.476	3.71	0.418
S	0.692	3.9	0.613
S	2.323	3.94	6.571
S	0.776	4.94	2.447
S	1.509	3.64	0.397
S	1.055	3.94	2.218
S	2.552	3.15	0.996
S	1.116	3.86	0.331
L	0.621	3.76	0.769
L	2.360	3.07	3.673
L	0.786	4.1	0.848
L	4.145	3.16	0.820
L	1.272	3.73	4.145
L	3.099	3.09	3.628
L	2.401	4.4	1.449
L	2.493	3.23	4.276
L	2.973	3.33	3.221
L	1.404	6.29	2.225
L	2.182	3.2	5.322
L	2.977	3	15.775
L	0.797	3.69	1.339
L	0.700	3.46	2.016
L	0.889	3.6	0.811
L	1.699	3.97	2.388
L	3.468	3.56	8.590
L	2.265	3.49	0.202
L	1.513	4.18	2.048
-	5.376	2.98	3.044
-	1.845	5.55	1.424
-	1.212	3.57	0.251
-	1.291	3.53	2.697

APPENDIX B
AGGREGATE DISPERSION ENERGY CURVES

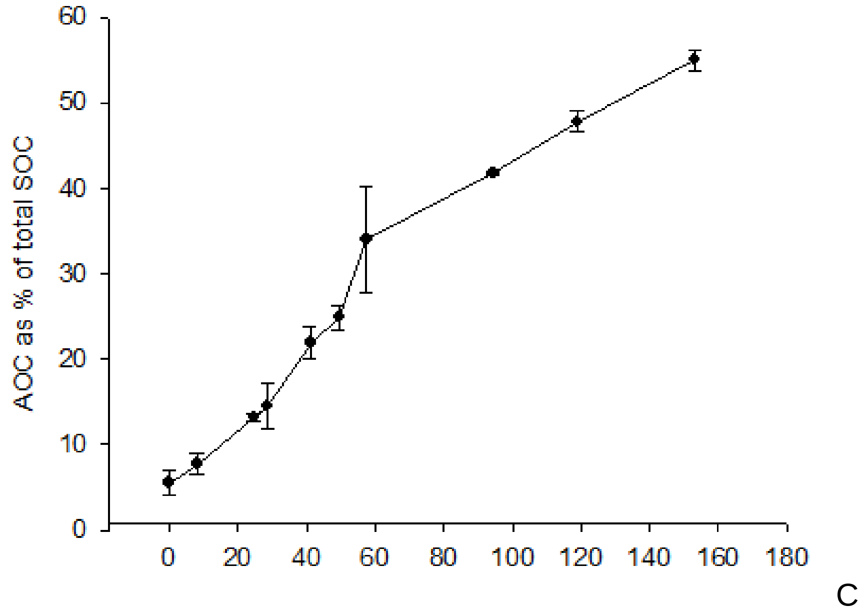


A



B

Figure B-1 Aggregate dispersion energy curve samples for loblolly pine ecosystem in aggregate organic carbon (AOC) as % of total soil organic carbon (SOC) by energy in JmL^{-1}.



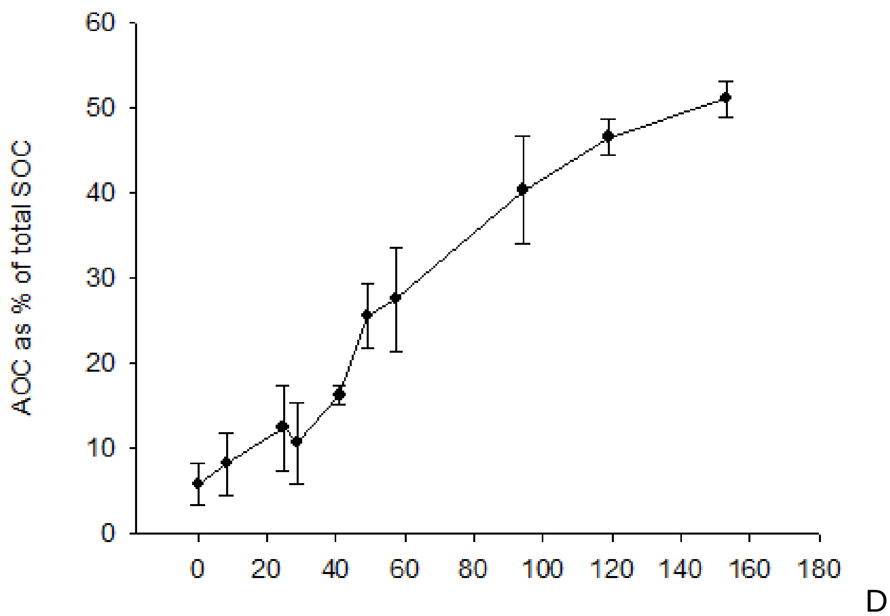
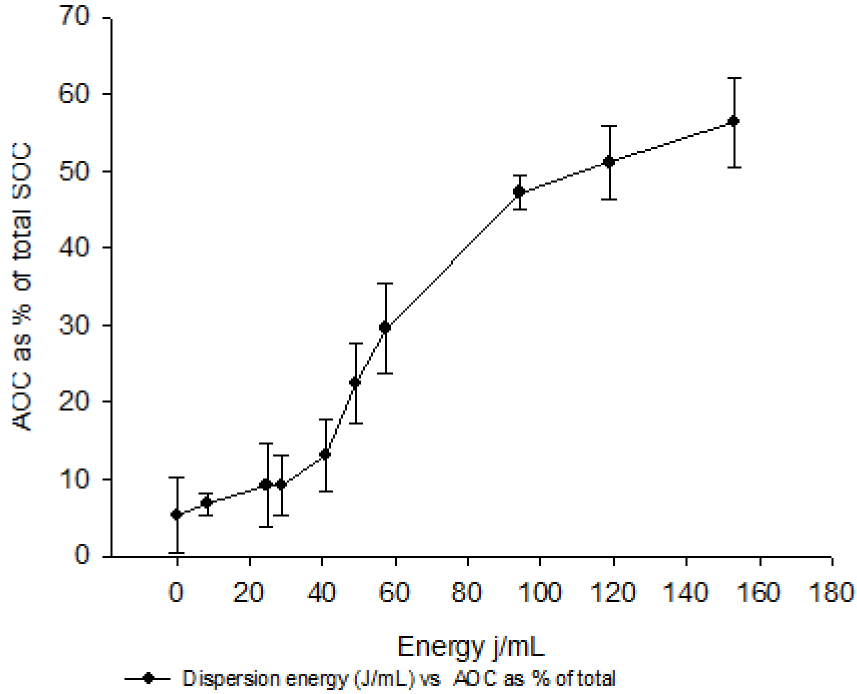
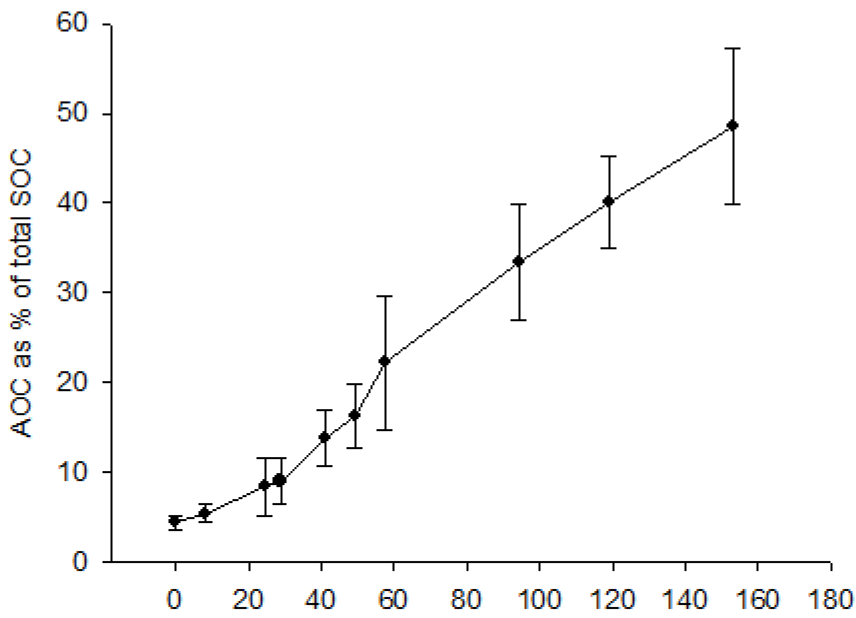


Figure B-1. Continued

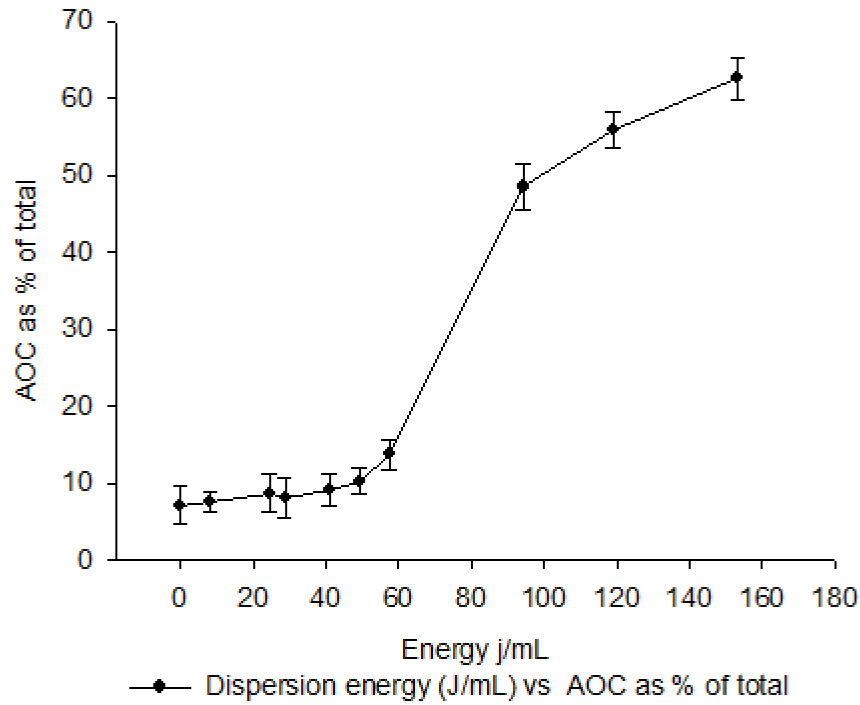


E



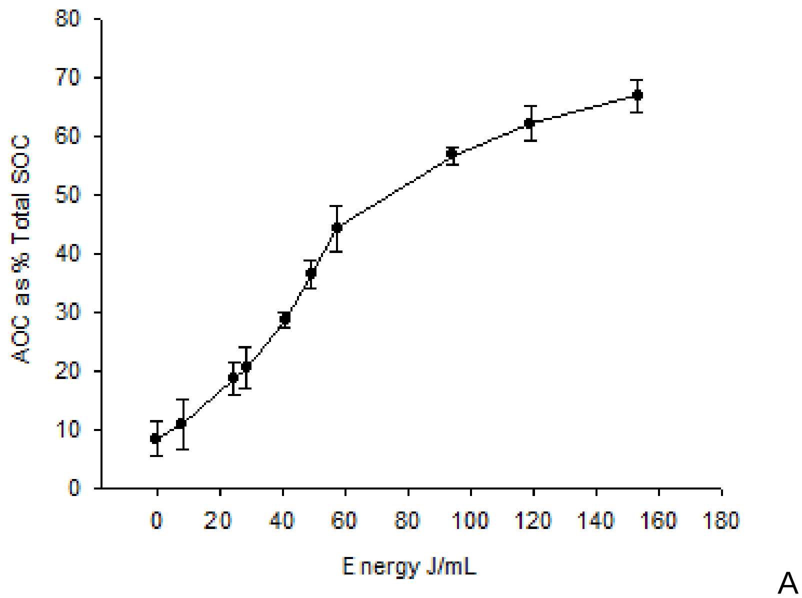
F

Figure B-1. Continued



G

Figure B-1. Continued



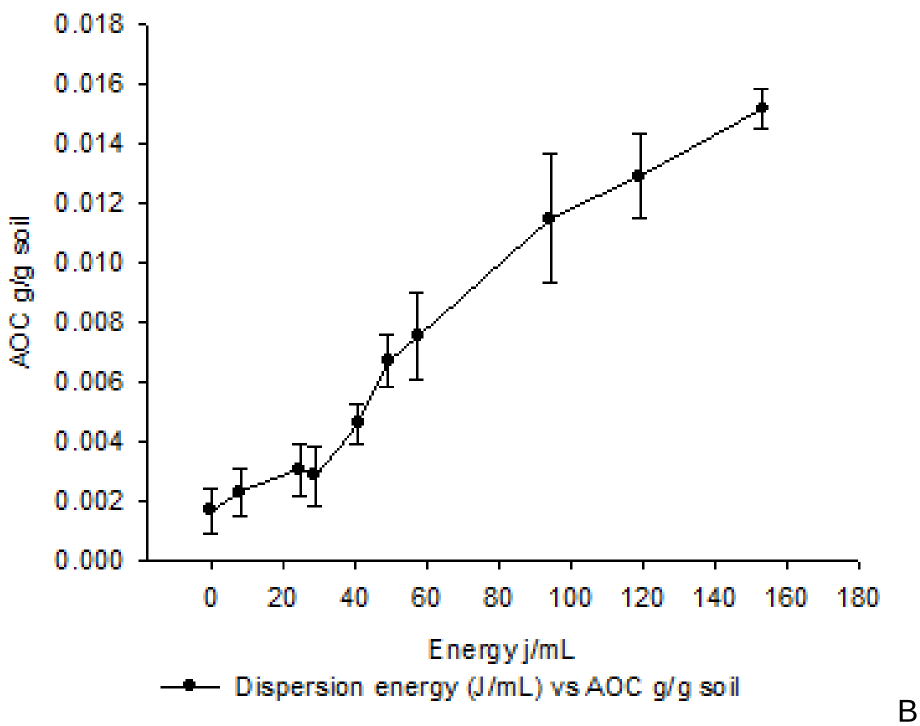


Figure B-2. Aggregate dispersion energy curves samples for slash pine ecosystem in aggregate organic carbon (AOC) as % of total soil organic carbon (SOC) by energy in JmL-1(Fig. A-F)

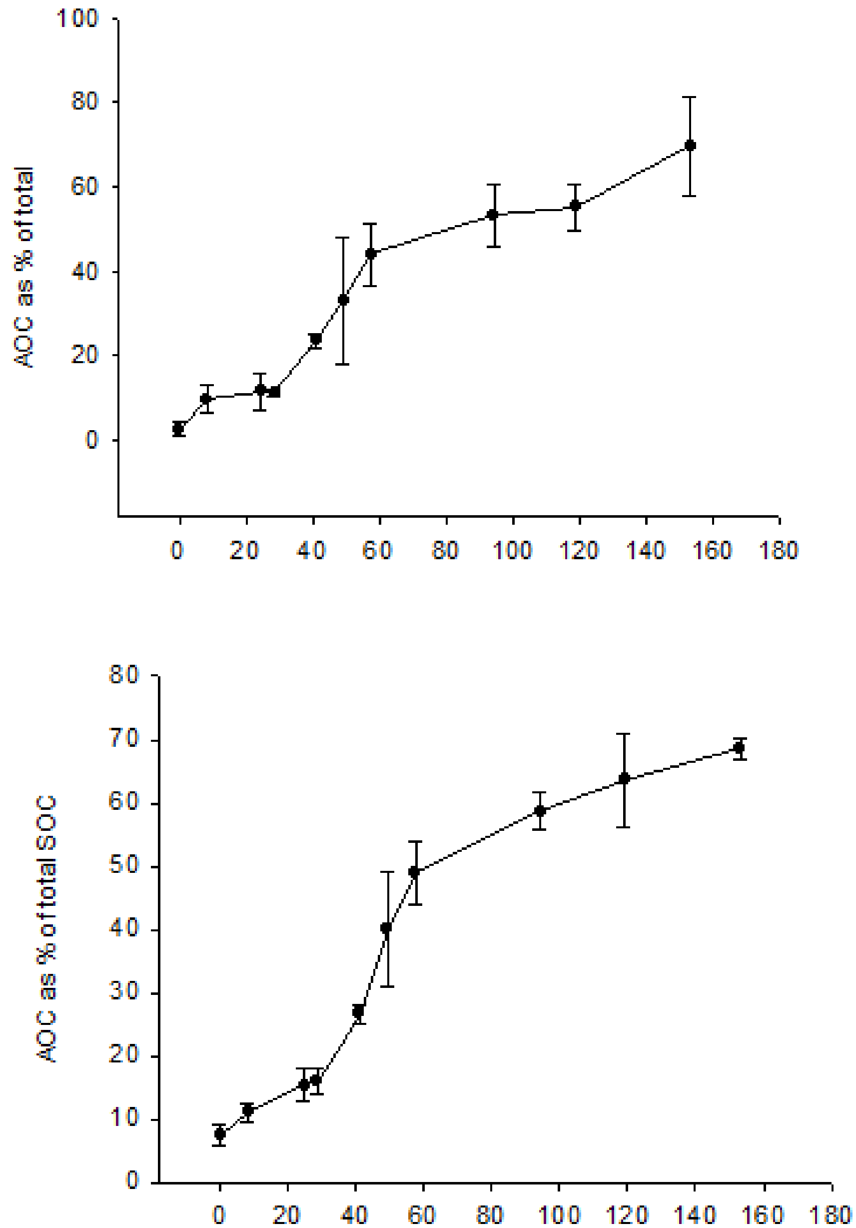
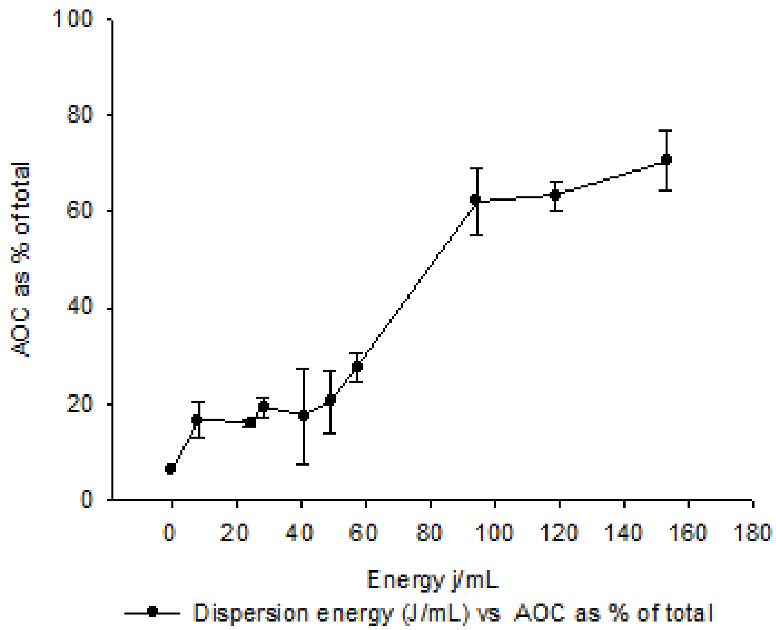


Figure B-2. Continued



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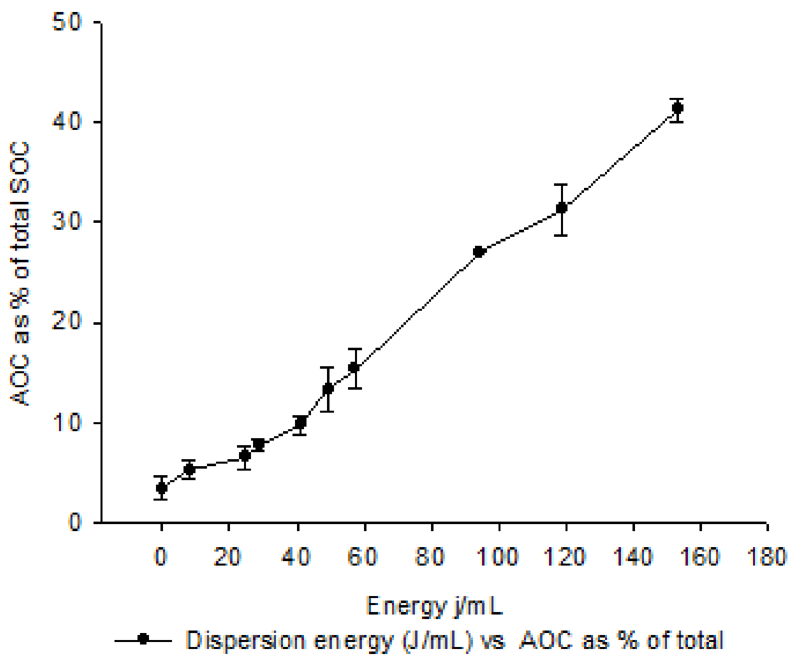
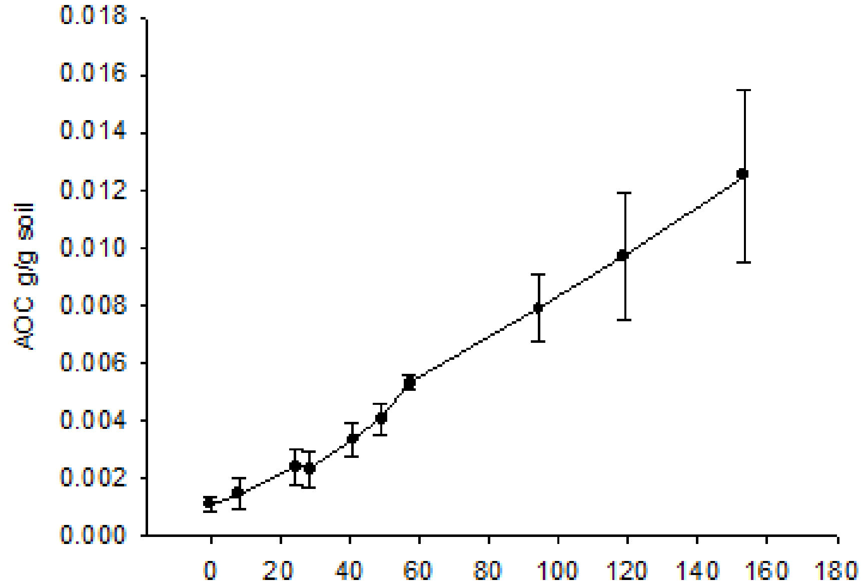
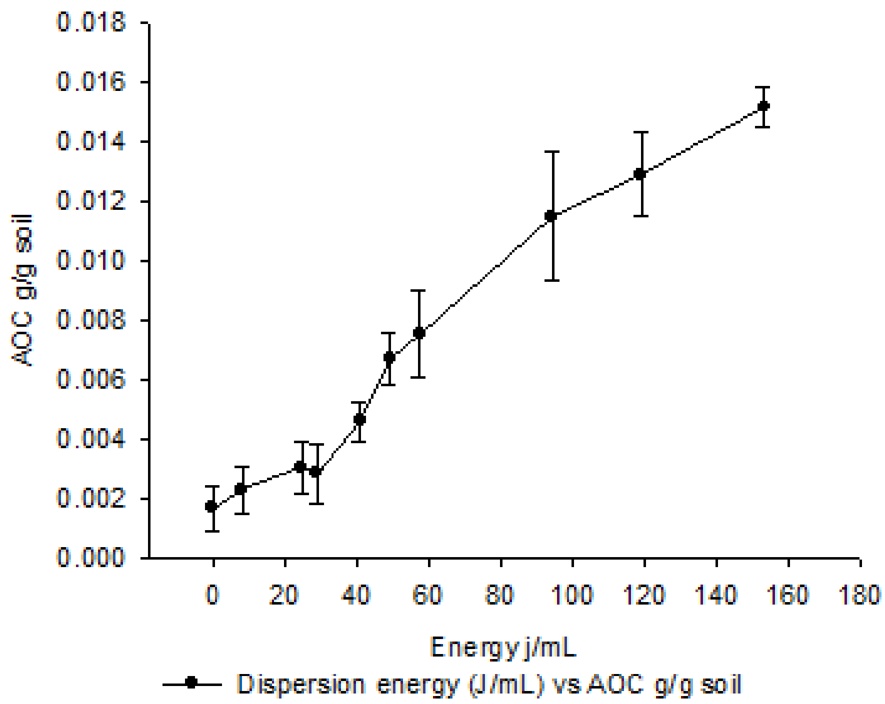


F

Figure B-2. Continued

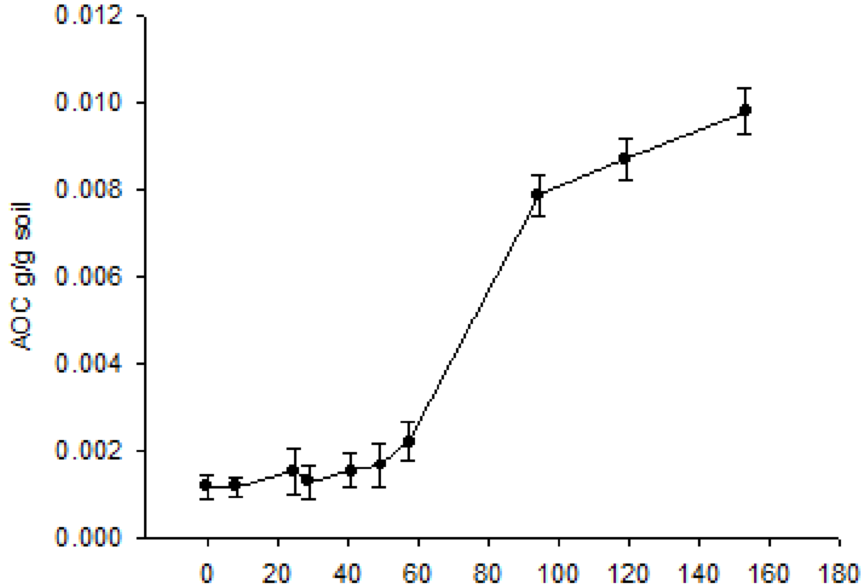


A

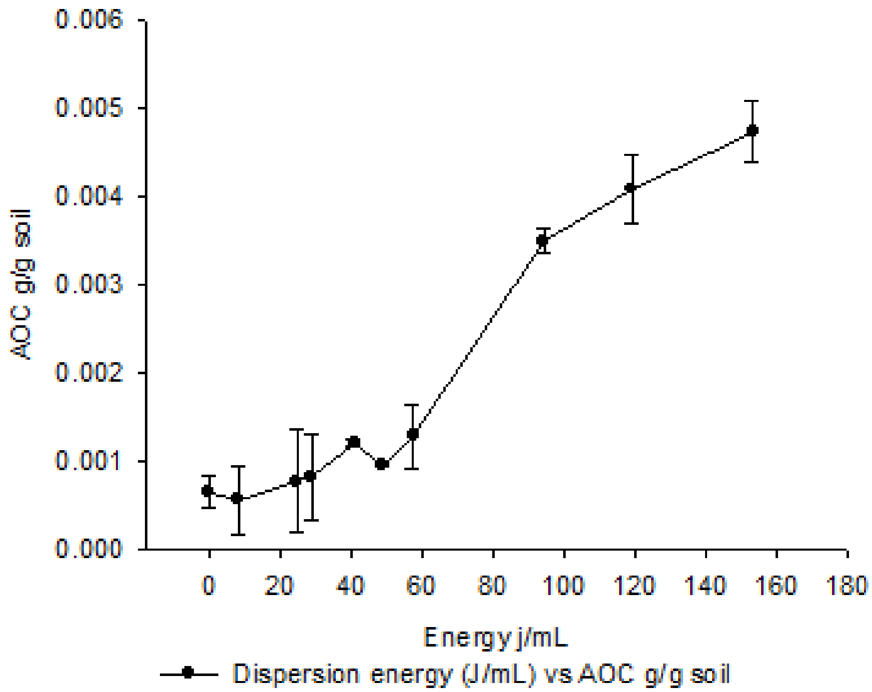


B

Figure B-3. Aggregate dispersion energy curve samples for loblolly pine ecosystem in aggregate organic carbon (AOC) g/g of soil by energy in J/mL (Fig. A-F)

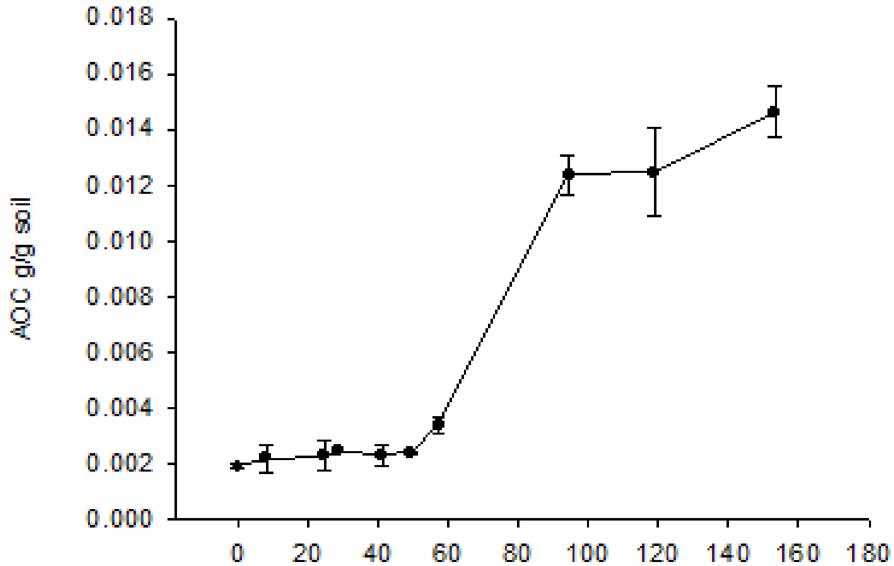


C



D

Figure B-3. Continued



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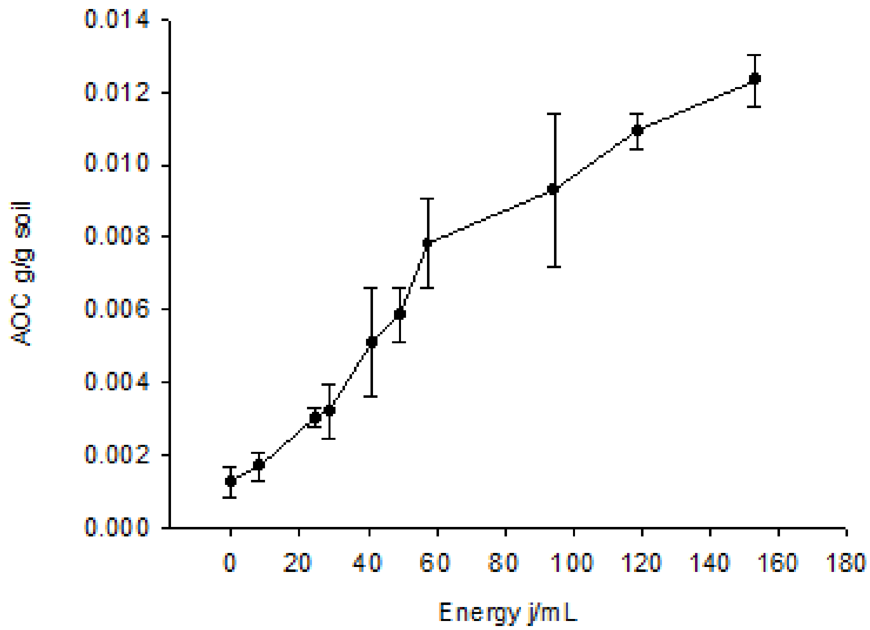


F

Figure B-3. Continued

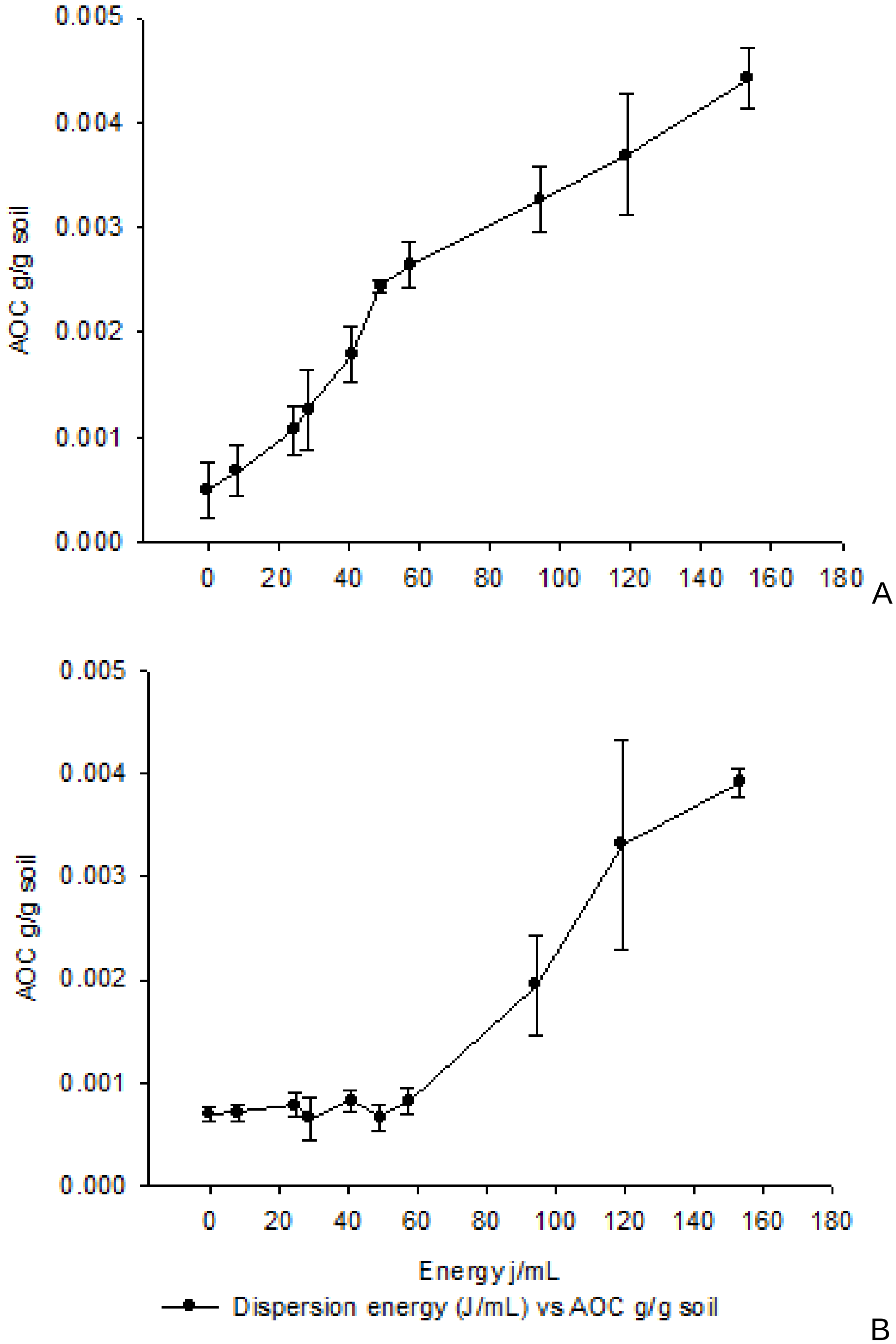
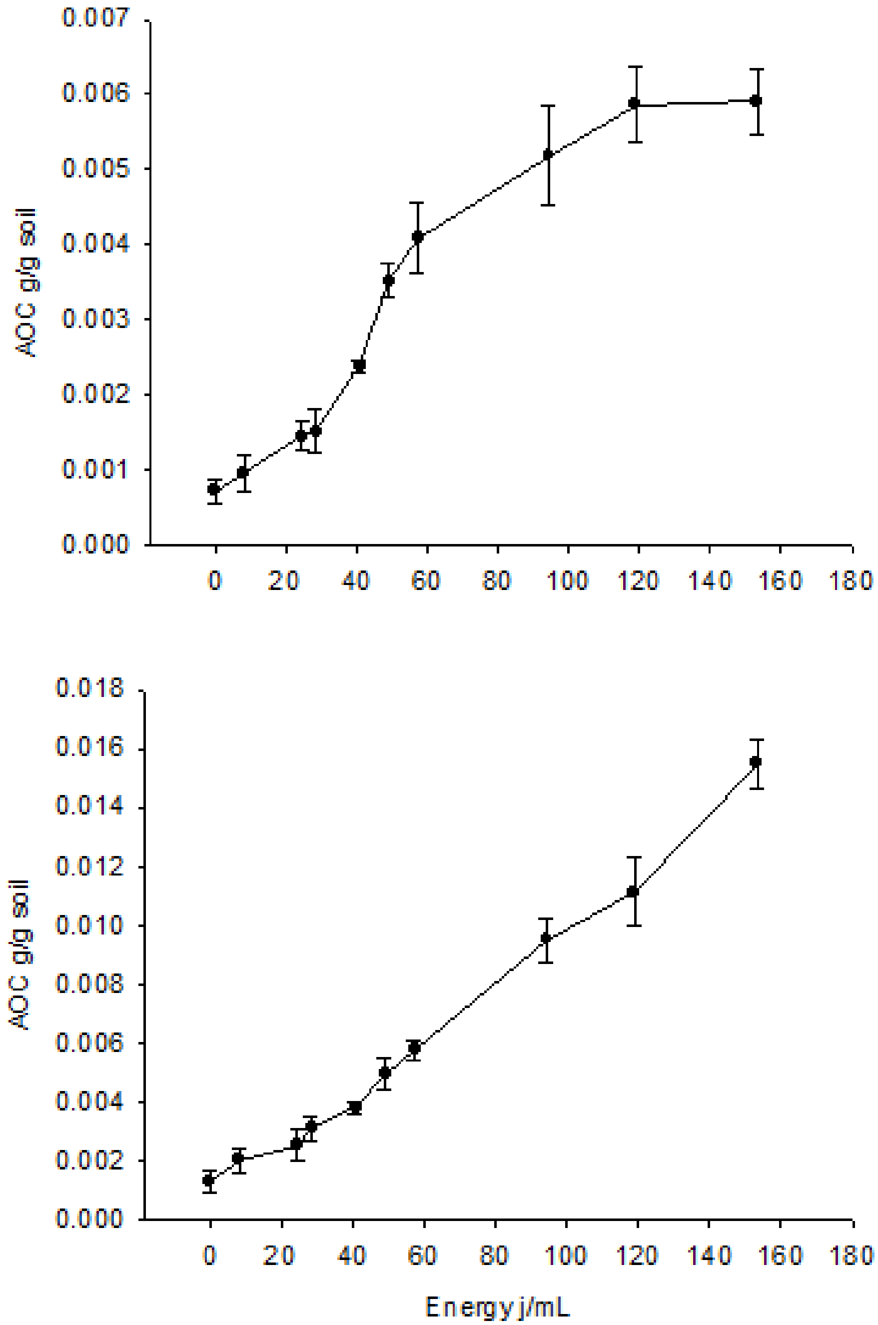


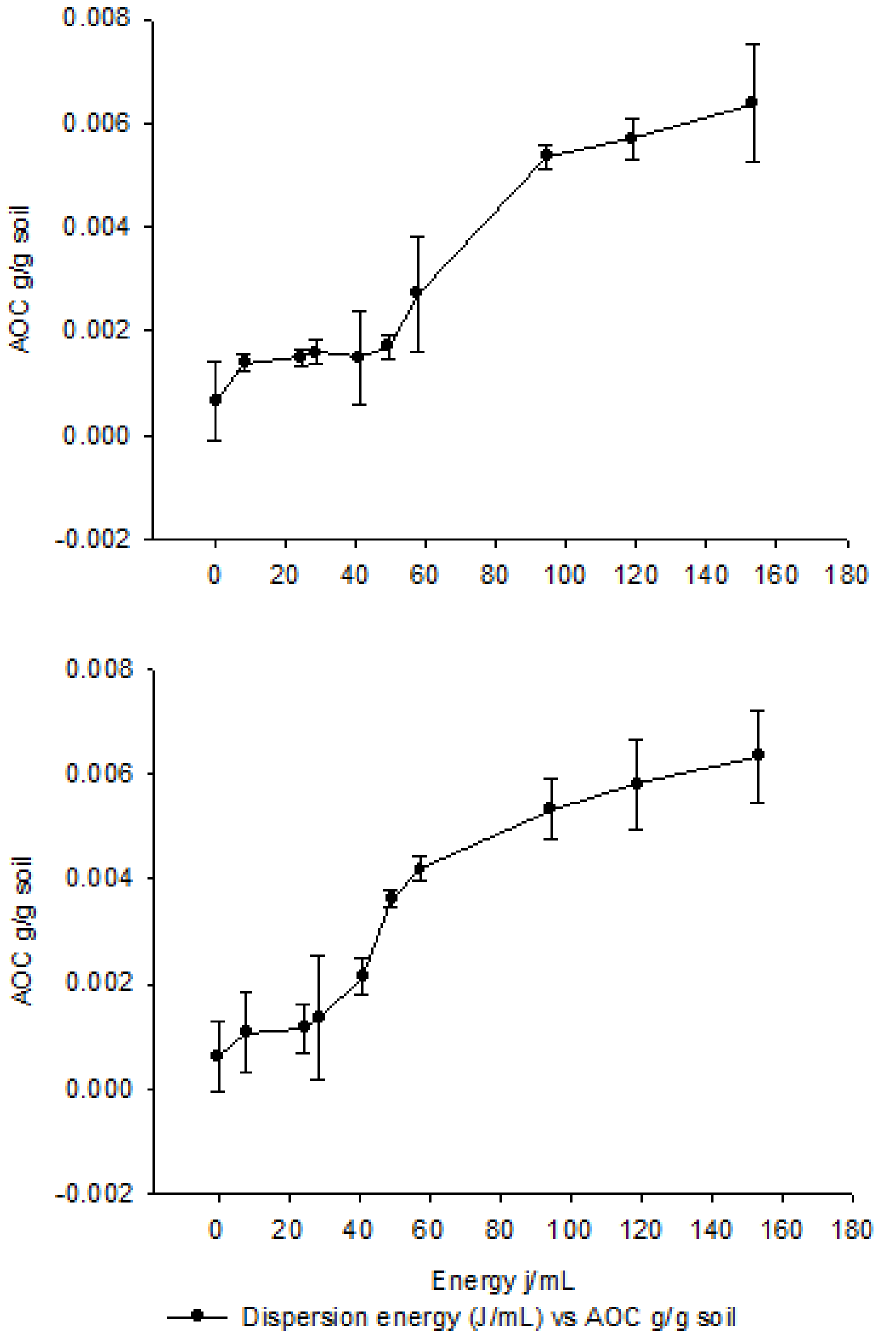
Figure B-4. Aggregate Dispersion Energy Curves samples for slash pine ecosystem in Aggregate Organic Carbon (AOC) g/g of soil by energy in J/Ml (Fig. A-F)



C

D

Figure B-4. Continued



E

F

Figure B-4. Continued

APPENDIX C
MID-INFRARED REFLECTANCE (MID-IR)

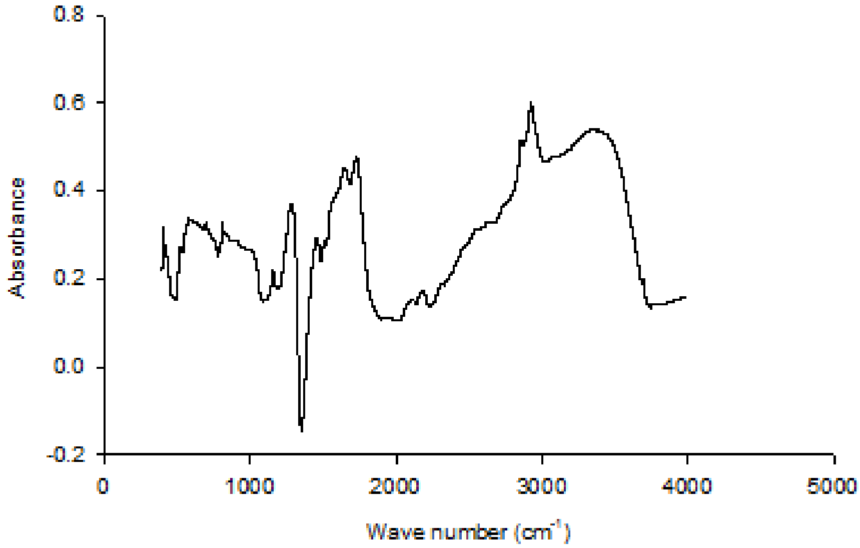


Figure C-1. Mid-infrared non-ashed spectrum average of loblolly pine influenced soil.

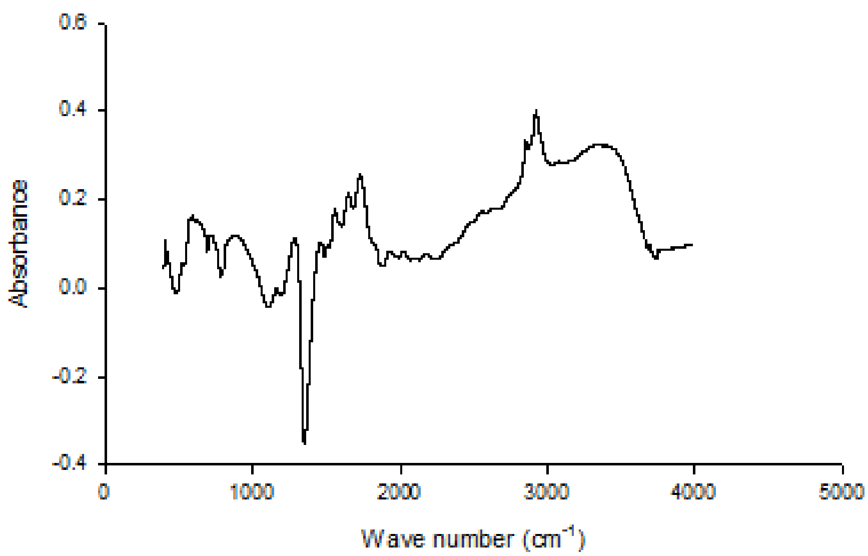


Figure C-2. Mid-infrared non-ashed spectrum average of slash pine influenced soil.

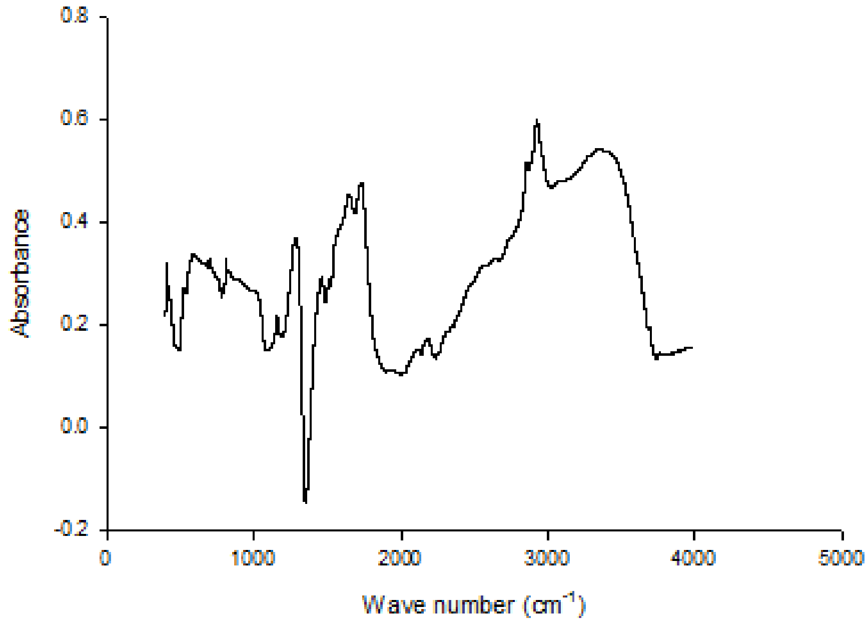


Figure C-3. Mid-infrared average spectrum of ash-subtracted loblolly pine influenced soil.

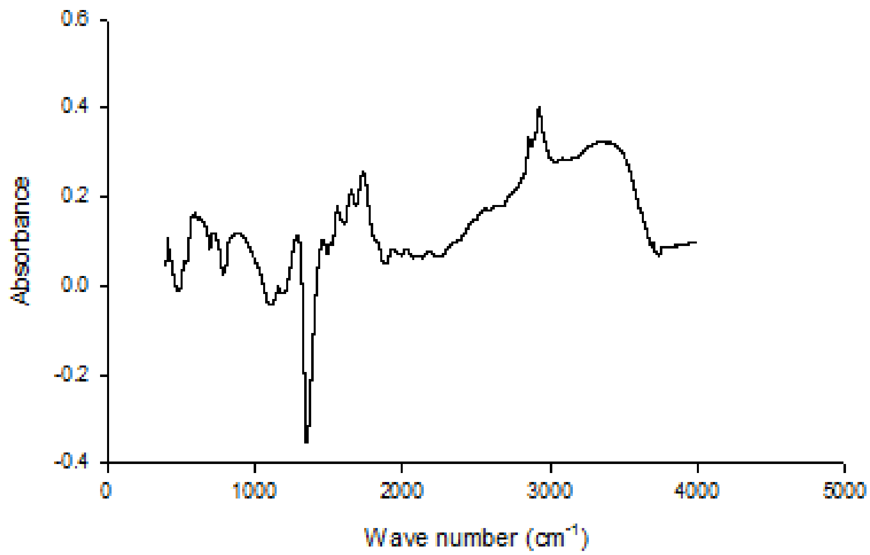


Figure C-4. Mid-infrared average spectrum of ash-subtracted slash pine influenced soil.

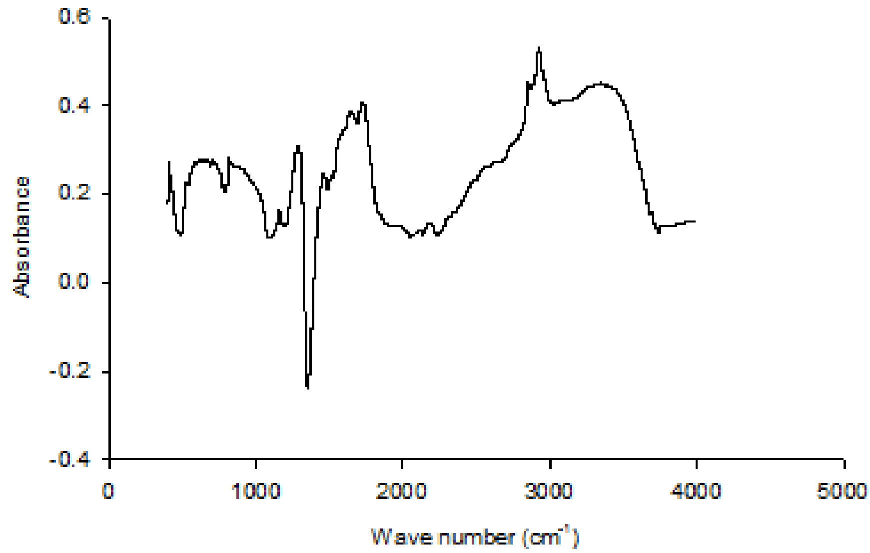


Figure C-5. Mid-infrared average spectrum of ash-subtracted loblolly pine influenced soils at week 29 of incubation study.

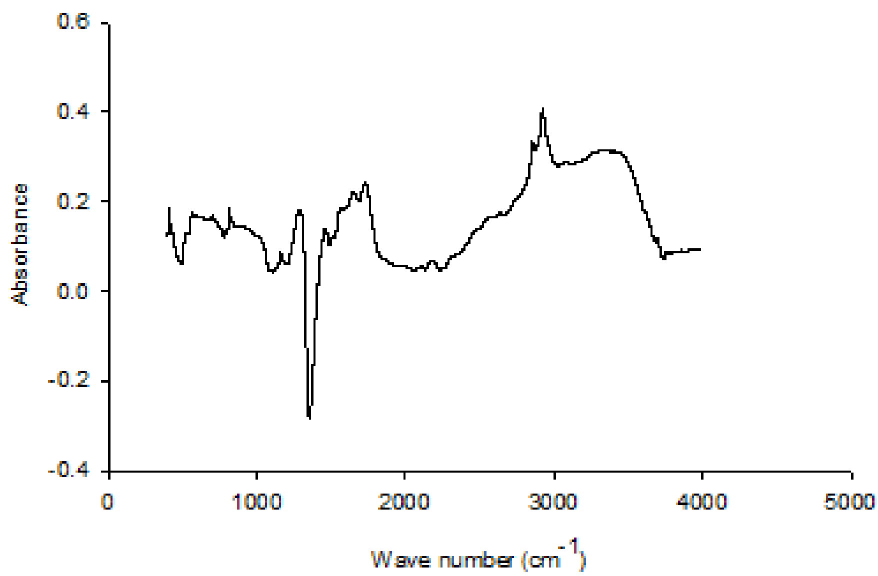


Figure C-6. Mid-infrared average spectrum of ash-subtracted slash pine influenced soils, at week 29 of incubation study.

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BIOGRAPHICAL SKETCH

The author was born in San Felipe, Venezuela. While raised between different family members (mom, dad, grandmother, and aunt), she had the opportunity to live in many places throughout childhood. As soon as high school ended she knew that an environmental career was her passion, however, in Puerto Ordaz, Venezuela the only colleges available had no environmental majors. As she started a major in sociology she became an entrepreneur by creating the first environmental group called MAWIDA at the Andres Bello Catholic University. She became recognized through this group and as a result the university granted her the opportunity to create and administrate a business (MAWIDA's café) that would provide a half scholarship for a student and also funds for the group. MAWIDA's café was a place from which she would impart environmental values through healthy meals, recycling and an eco-friendly environment. Although she was satisfied with her accomplishments, Elena knew she had to expand her knowledge in order to be able to convey environmental awareness. She then made the decision to transfer to Valencia community college in the United States as she prepared herself to begin at the University of Florida completing a bachelor in forest resources and conservation. In her senior year while working as a laboratory assistant for the forest soils laboratory, she started a combined degree to acquire a master's degree in soil and water science.