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## Loblolly and slash pine control organic carbon in soil aggregates and carbon mineralization

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### ABSTRACT

The influence of soil aggregation as a means to protect soil organic carbon (SOC) from mineralization is unclear in very sandy soils. The dominant forest cover types in the Lower Coastal Plain of the US where sandy surface soils prevail are loblolly pine (*Pinus taeda*) and slash pine (*Pinus elliottii* var *elliottii*). The purpose of this study was to investigate the role that aggregation plays in C incorporation and sequestration in very sandy soils of the Lower Coastal Plain found under loblolly and slash pine ecosystems. Thirteen forest stands (seven loblolly pine; six slash pine) were used for this investigation. A sonic dismembrator was used to apply dispersive energy in order to destroy aggregates. The use of sonic energy was shown to be a valid tool for studying aggregates in sandy soils. The data showed that aggregates do not protect ASOC from mineralization in these very sandy soils. Loblolly pine surface mineral horizons accumulated 131% more TSOC than slash pine soil horizons. Slash pine soils had a 27% higher specific mineralization rate than loblolly pine soils; and Diffuse Reflectance Fourier Transform spectra (DRIFTS) showed that soils under loblolly pine were more aromatic than those under slash pine – and became more aromatic as mineralization proceeded. Due to their dominance in the Lower Coastal Plain of the US, pine ecosystems play an important role in the conversion of atmospheric CO<sub>2</sub> into the TSOC pool. However, soil aggregation should not be considered a mechanism to protect SOC in these very sandy soils when modeling soil carbon dynamics, even though slash pine systems show a slightly greater capacity to develop aggregates.

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### 1. Introduction

Soil aggregation reduces erosion, improves water infiltration, and protects aggregate soil organic carbon (ASOC) from mineralization (Lal et al., 1997). Yet one relevant question is whether the protection function is equally true for all soil textures. The ASOC is protected physically, chemically and physiochemically (Golchin et al., 1994; Blanco-Canqui and Lal, 2004), with ASOC turnover rates appearing to be faster in macroaggregates than microaggregates. According to Besnard et al. (1996), Franzluebbers and Arshad (1997) and Sainju et al. (2003), this suggests greater protection of ASOC by microaggregates. Wild (1988) further suggested that ASOC in microaggregates may also be better protected if it is more biochemically recalcitrant. These observations have resulted in the commonly held belief that the C storage provided by macroaggregates is greater in quantity but transient in terms of

physical protection compared to microaggregates (Tisdall and Oades, 1982).

The ability of soils to physically protect soil C through aggregation appears to be partially dependent on soil texture. Residence times of ASOC in macro and microaggregates differ depending on the physiochemical attraction between mineral and organic particles, and the location of the organic material within the aggregates (Emerson, 1959). Buyanovsky et al. (1994), working with a silt loam soil under soybean cultivation, found that turnover rates of ASOC were 1–3 years for macroaggregates and approximately 7 years for microaggregates. Conversely, Skjemstad et al. (1990) found no remarkable difference between the ASOC turnover rates of macro and microaggregates in an Australian sandy soil. Christensen (1987), working with loamy sand and sandy loam soils noted no physical protection of ASOC due to aggregation. This evokes the question: what level of physical protection does ASOC have in sandy soils?

Aggregate dispersive energy (ADE) has been used to characterize aggregate strength in a variety of soils. One assumes that ADE relates to ASOC protection; however, the relationship between ADE and C mineralization within aggregates has been poorly

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studied. 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. The ADEC method has the potential to quantify the ASOC that is physically protected (North, 1976; Christensen, 1992; Cambardella and Elliot, 1993; Six et al., 2001; Swanston et al., 2005; Sarkhot et al., 2007a). One method of dispersing aggregates uses sonic energy (Sarkhot et al., 2007a), yet there have been no studies that document the degree of aggregate dispersion via sonic vibrations.

As mentioned above, sandy soils have been studied for their amount and properties of micro and macroaggregates, yet their ability to protect ASOC has been poorly documented (Sarkhot et al., 2007a). Sandy surface soil horizons dominate in the Lower Coastal Plain of the Southeastern US. These and associated flatwood soils make up 25% of the land base of Florida (Zelazny and Carlisle, 1971) or over 3.4 million ha. Sarkhot et al. (2007a,b), presenting the only ADECs published for Lower Coastal Plain soils, demonstrated that these very sandy soils (less than 5% clay) were well aggregated, showed a hierarchical aggregate structure, and showed that they held as much as 40% or more of the total soil organic carbon (TSOC) as ASOC. However, no information exists on the stability of ASOC relative to ASOC mineralization for these important agricultural and forested soils.

Fourier Transform Infrared Spectroscopy (FTIR) has been useful in investigating soil organic carbon changes due to soil management and land use changes. Ellerbrock and Kaiser (2005) showed that crop and site conditions controlled the chemical signature of organic matter fractions. Sarkhot et al. (2007a) used a form of FTIR, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), on a soil similar to the one used in this study to identify TSOC chemical differences in different soil size fractions and TSOC changes due to dry and wet sieving. DRIFTS should be a useful measure in evaluating TSOC and ASOC chemical fingerprints.

The purpose of this study was to investigate the role that aggregation plays in C incorporation and sequestration in very sandy soils of the Lower Coastal Plain found under loblolly and slash pine ecosystems. This was addressed by focusing on four objectives: (i) validation of a sonication method for determining ADECs; (ii) comparison of TSOC incorporated into aggregates of the sandy surface horizon of loblolly and slash pine ecosystems; (iii) examination of the relationship between ADE and TSOC and ASOC accumulation and mineralization for loblolly and slash pine ecosystems, and (iv) identification of TSOC chemical characteristics via DRIFTS that explains differences in TSOC stability and mineralization.

## 2. Methodology

### 2.1. Experimental sites and field sampling

The experimental sites and samples from these sites were chosen from a previous stratified random sampling study which was geared toward developing a soil carbon inventory of the state of Florida based on 1000 sampling points throughout the state. The study area used for this research was National Resource Conservation Service – Conservation Area 2 located in North Florida. From the original set of 55 forest stand locations in this Conservation Area, 13 sites were selected. Seven sites supported loblolly pine (*Pinus taeda* L.) ecosystems and 6 sites supported slash pine (*Pinus elliottii* var *elliottii* Engelm.) ecosystems. Originally seven slash pine sites were selected but it was later found that one site was misclassified, so it was removed from the data set. The sites were chosen so that they had similar soil C means and the ranges that were characteristic of the original set of 55 locations. The TSOC means and ranges were 1.06% and 4.01% for slash pine sites and 2.45% and 1.17% for loblolly pine sites. A soil sample from the surface

20 cm of mineral soil was collected at each sampling location by combining four 30 × 5.8 cm cylindrical cores (McIntyre, 1974). Soils were then air-dried and sieved to pass a 2 mm screen.

Sampling sites were located in the North Florida counties of Alachua, Citrus, Clay, Duval, Flagler, Lafayette, St. Johns, Putnam, Taylor, and Volusia. The climate of the region is hot and humid with an average yearly precipitation of 113 cm, and yearly average minimum and maximum temperatures of 14 °C and 27 °C (South-east Regional Climate Center, 2007). The sampling sites represented Flatwood landscapes which are somewhat poorly to poorly-drained with a seasonally high water table. Because the sites were randomly selected from all possible sampling points in the conservation area, the past history of each is unknown. However, because of the sampling scheme, these sites are representative of field conditions in the Conservation Area. All soils but one were Spodosols represented by the Suborder, Aquod (Table 1). Loblolly and slash pine ecosystems had a common understory of saw palmetto (*S. Serenoa repens* Small), wax myrtle (*Myrica cerifera* L.), gallberry (*Ilex glabra* L.), brackenfern (*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.), sweetgum (*Liquidambar styraciflua* L.), bays (*Persea* sp.), and Florida maple (*Acer barbatum*). One loblolly and one slash pine site were natural pinelands following disturbance; while the remaining were under plantation management. All stands were 8–15 years in age.

### 2.2. Laboratory methods

#### 2.2.1. Experiment 1. Testing of the sonication method

The sonication method used to develop aggregate dispersion energy curves (ADEC), as defined by Sarkhot et al. (2007a,b), was tested on each soil size fraction. The purpose of this experiment was to assure that sonication resulted in aggregate dispersion. The evaluation was done on three soil size fractions. These size fractions were consistent with those used in other studies (Oades and Waters, 1991; Roscoe et al., 2000; Six et al., 2001; Sarkhot et al., 2007a). One 100 g soil sample from the surface of a Spodosol, similar to the sampling sites in this study, was dry-sieved through a horizontal mechanical shaker for 5 min at 75 rpm using 53, 150, and 250- $\mu$ m sieves (Sarkhot et al., 2007a). Therefore, the resulting size fractions used in this study were 2000–250, 250–150, and 150–53  $\mu$ m. The less than 53  $\mu$ m fraction was not used.

The ADEC for each size class sample was constructed by the method of Sarkhot et al. (2007a,b). Six, 5-g samples of each size class were placed into glass beakers with 100 mL of deionized water. Each of the 5-g sample was exposed to a unique, increasing energy level (0–200 J mL<sup>-1</sup>). Using a sonic dismembrator (Fisher Scientific, Model 500, Hampton, NH), the sonic probe was immersed 10 mm below the surface of the suspension. Energy levels were applied by using a range of amplitude (20–69%) and time (1–7 min) combinations. A correction factor was applied to the energy levels, as described by Sarkhot et al. (2007a), to adjust the readings for energy absorbed by the water and lost as heat. Temperature rise was minimized 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 and ASOC that resisted dispersion. The SOC passing through the sieve was considered the ASOC that was dispersed by sonication. Sieve retentates were dried in a forced-air oven at 65 °C. Three 0.1 g subsamples of the oven-dried retentates were placed under a microscope and the numbers of aggregates were counted with the help of a 1 cm × 1 cm grid system.

**Table 1**

Location, pine species and soil taxonomic classification of the North Florida loblolly and slash pine sites used in the study.

County	Pine species	Latitude	Longitude	Soil taxonomic classification
Alachua	Loblolly	29.711580	–82.343671	Hyperthermic Ultic Alaquod
Duval	Loblolly	30.465195	–81.530360	Thermic Typic Alaquod
Lafayette	Loblolly	30.017988	–83.302321	Thermic Aerlic Alaquod
St. Johns	Loblolly	29.858920	–81.361572	Hyperthermic Ultic Alaquod
Taylor	Loblolly	29.866656	–83.418372	Thermic Alflic Alaquod
Taylor	Loblolly	29.836545	–83.428403	Thermic Spodic Psammaquent
Flagler	Loblolly	29.486148	–81.317456	Hyperthermic Aerlic Alaquod
Clay	Slash	30.159932	–81.945865	thermic Ultic Alaquod
Clay	Slash	29.891132	–81.853681	Thermic Aerlic Alaquod
Lafayette	Slash	30.017128	–83.154864	Thermic Ultic Alaquod
St. John's	Slash	30.088603	–81.534517	Hyperthermic Typic Alaquod
Clay	Slash	29.849814	–81.663151	Thermic Aerlic Alaquod
Volusia	Slash	29.206476	–81.512600	Hyperthermic Aerlic Alaquod

### 2.2.2. Experiment 2. Aggregate dispersion energy curves

This experiment developed ADECs for each sample site and was based on soil material greater than 53  $\mu\text{m}$  and less than 2 mm. This is in contrast to developing ADEC by sizes fractions as tested in Section 2.2.1 and as previously reported in other studies on similar soils (Sarkhot et al., 2007a,b). The intent of the ADECs in this experiment was to develop a curve to represent all aggregates in a soil sample. Each soil sample was dry-sieved through a horizontal mechanical shaker for 5 min at 75 rpm using a 53  $\mu\text{m}$  sieve (Sarkhot et al., 2007a). The result was subsamples between 2000  $\mu\text{m}$  and 53  $\mu\text{m}$  in size.

Three replicate ADECs were developed for each of the 13 sites. Five grams of sieved sample were weighed into a 250 mL Dewar vessel and combined with 100 mL of deionized water. The samples were arranged so that 6 energy levels between 0 and 153  $\text{J mL}^{-1}$  were evaluated for each size class of each soil sample. The sonic probe was lowered into the sample and maintained at a constant depth of 12 mm into the suspension. Sonication was accomplished as described in Section 2.2.1. The 153  $\text{J mL}^{-1}$  upper level was selected based on the sonication test described in Section 2.2.1. The energy dissipated into the suspension was calculated using a correction factor to adjust the energy level applied to the aggregates as described by Sarkhot et al. (2007a,b). This actual energy was calibrated calorimetrically with a Dewar vessel as described by Schmidt et al. (1999). After each subsample was sonicated, it was wet-sieved through the 53  $\mu\text{m}$  screen. The material on the screen and that passing through the screen was subjected to loss-on-ignition (LOI). Soil C was determined for the LOI by applying a conversion factor based on unpublished data that correlated 133 measurements of SOC measured with LOI for Spodosols across a watershed in N. Florida. The conversion was  $\text{SOC} (\%) = 0.4922 * \text{LOI} (\%) + 0.065$  with an  $R^2$  of 0.84.

### 2.2.3. Experiment 3. Mineralization of AOC at three points on the ADEC

**2.2.3.1. Part 1. Soil mineralization.** An incubation study was used to ascertain if the ADE of aggregates was a factor in ASOC mineralization/protection. To that end, a microcosm for each soil sample was constructed. Each microcosm contained 20 g of soil, 0.05 g of soil inoculum and a liquid base trap of 20 mL of 0.25 M NaOH. The soil inoculum was added to assure a microbial population that may have been eliminated due to the sonic energy application. The SOC added with the inoculum was miniscule with respect to the SOC measurements and was therefore ignored. Each site used in this study was represented by nine microcosms that reflected three replications of three treatments. The treatments were (i) no energy applied, (ii) energy applied at 58  $\text{J mL}^{-1}$ , and (iii) energy applied at 153  $\text{J mL}^{-1}$ .

Since sonication required soil saturation, each sample was filtered after sonication through a 0.22  $\mu\text{m}$  membrane via a vacuum

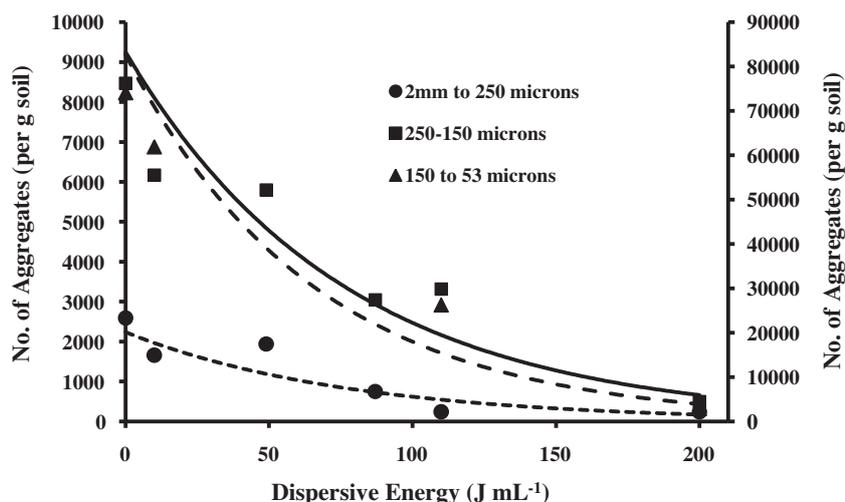
system at a pressure of 0.33 bars (Schwesig et al., 2003). Sonication suspended dissolved organic carbon (DOC) making it part of the filtrate. A subsample of the filtrate was analyzed for DOC using a Shimadzu TOC-VCPH Analyzer (Shimadzu Scientific, Columbia, MD). The remaining DOC was used in the second mineralization experiment described in Section 2.2.3.1.

The mineralization microcosms were placed in an incubator at 35 °C. The water content was maintained at 0.33 bars, 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 method as described by Anderson (1982) was used to determine the rate of carbon dioxide ( $\text{CO}_2$ ) evolution.

**2.2.3.2. Part 2. DOC mineralization.** The DOC is part of the ASOC and responsible for some fraction of the mineralizable TSOC. The range in DOC concentration was 0.08 to 0.57  $\text{mg g}^{-1}$  soil. In order to determine the mineralization rates of the DOC released by sonication, 60 mL of the DOC solution described in Section 2.2.3.1 were added to a 250 mL Erlenmeyer flask which held 0.05 g of soil inoculum. The C added by the inoculum was insignificant relative to DOC levels. These samples were mineralized in the dark at 35 °C for 84 days. The  $\text{CO}_2$  evolved was measured as detailed in Section 2.2.3.1. Due to the small portion that DOC represents of the TSOC, and due to the lack of differences between mineralization of DOC based on species and dispersion level, the mean DOC mineralization rate was used to calculate the DOC mineralized over time for each treatment. This value was added to the carbon mineralization measured in Experiment 3 Part 1 in order to provide the best estimate of TSOC mineralized from each treatment.

### 2.2.4. Experiment 4. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS)

The utility of DRIFTS is based on its sensitivity, spectral precision, reproducibility and fast spectral acquisition time (Johnston and Aochi, 1996). This method was used to describe the organic C present by: species, incubation periods and dispersion energy levels. DRIFTS used the mid-infrared (mid-IR) spectral region (4000–400  $\text{cm}^{-1}$ ). Spectra were analyzed on a Digilab FTS-7000 FTIR instrument (Varian, Inc., Walnut Creek, CA). Samples were placed in a Pike AutoDiff 60-cup autosampler (PIKE Technologies, Madison, WI). Ground and ball-milled samples were placed in the autosampler cups and scanned using a KBr beam splitter and deuterated triglycine sulfate (DTGS) detector. The sample (unashed) plus the ash of the sample following LOI were run to derive spectra. Spectral subtraction of ashed samples from unashed samples was used to emphasize the organic composition. This subtraction was accomplished using GRAMS/AI software, Version 7.02 (Thermo Galactic, Salem, NH; Sarkhot et al., 2007a). Spectra by



**Fig. 1.** The number of soil aggregates per gram of soil left after the application of increasing levels of dispersive energy (sonication) applied to each of three soil size classes: 2000–250  $\mu\text{m}$ , 250–150  $\mu\text{m}$  and 150–53  $\mu\text{m}$ . The two larger size classes are graphed with the left y-axis and the lowest size class is graphed with the right y-axis. Each trend line is an exponential fit to the data.

species were averaged from the ash-subtracted spectra from each site, and graphed to observe the differences due to species, 1 and 29 weeks after mineralization, and dispersion energy levels. Functional group identification analysis was performed with the support of IR Analyze software (Version 3.0.1.9.0, 2008, LabCognition, GmbH and Comp., Cologne, Germany).

### 2.2.5. Statistical analysis

Experiment 2 was analyzed with a completely randomized covariance analysis design where the independent variables were energy level and pine species. Dependent variables were the amount of ASOC expressed as ASOCg ( $\text{g g}^{-1}$  soil) and ASOC% (ASOC as a percent of TSOC). The covariate was TSOC to account for inherent variability between sampling sites. The dependent variables required log transformations before analysis. All figures were made from back-transformed data for ease of understanding. When significant main effects or interactions were found, post hoc multiple mean comparisons were evaluated using Tukey's procedure. Effects were considered significant if  $p < 0.05$ , and a  $p < 0.10$  was considered a trend worth noting.

For Experiment 3, the analysis was run on the mineralization data for TSOC (where the results of DOC mineralization were included). The analysis was a repeated-measures ANOVA where the main effects were species and energy level for each measurement date and the dependent variable was weekly mineralization in  $\text{mg C respired g soil}^{-1}$ . Differences were considered significant if  $p < 0.05$ . When significant main effects or interactions were found, Tukey's post hoc multiple mean comparisons procedure was applied. The amount of DOC released by sonication was analyzed by an analysis of covariance. The covariate was TSOC and the main effects were species and energy level. All statistical analyses were run using STATISTICA (Statsoft, Inc. 9.0; Tulsa OK).

## 3. Results

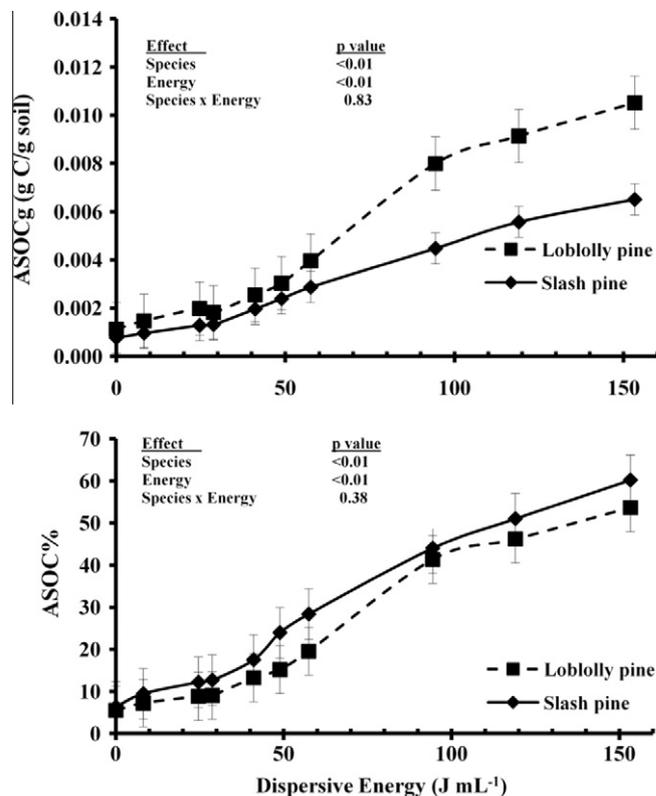
### 3.1. Objective 1. Sonication method

The number of aggregates per gram of soil increased with decreasing size fraction (Fig. 1). The 2000–250  $\mu\text{m}$  soil size fraction was fully dispersed at the 100  $\text{J mL}^{-1}$  energy level. The two smaller size fractions required 150–200  $\text{J mL}^{-1}$  for complete dispersion; with the inflection point appearing around 150  $\text{J mL}^{-1}$  (Fig. 1). Microscopic observations of aggregates indicated that macro and

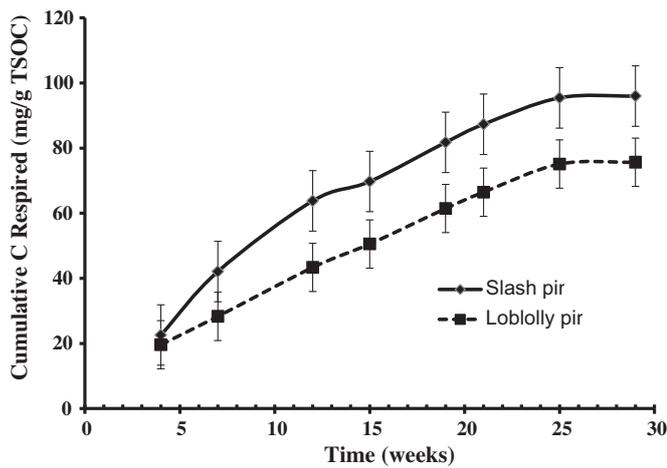
microaggregates in all size fractions were characterized by the incorporation of fungal hyphae and fine roots within the aggregate organic matrix. Other materials among the aggregates were fecal pellets, root epidermis and insect carcasses.

### 3.2. Objective 2. Aggregation in loblolly and slash pine soils

The TSOC of the surface mineral horizon under loblolly pine was significantly higher (131% higher) than that under slash pine (2.36% vs. 1.02%). The variables ASOCg and ASOC% were influenced

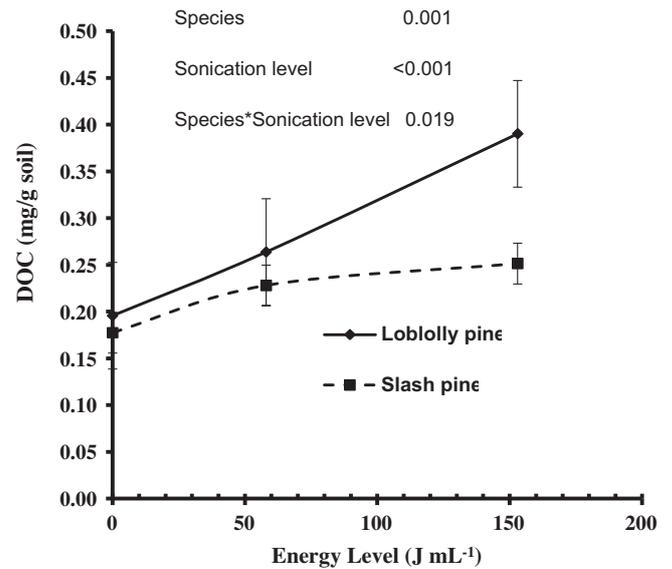


**Fig. 2.** Cumulative aggregate soil organic carbon (ASOC) in soils as influenced by loblolly and slash pine and measured by applying aggregate dispersive energy through sonication. ASOC is expressed as (a) the amount of ASOCg (ASOC per gram of soil) and (b) ASOC% (ASOC as % of TSOC). The bars are standard errors.



**Fig. 3.** Cumulative soil C respired over time from the  $0 \text{ J mL}^{-1}$  dispersive energy treatment ( $<2 \text{ mm}$  to  $>53 \text{ }\mu\text{m}$  soil size class) for soil under loblolly and slash pine ecosystems. The C respired is expressed as mg of C per gram of total soil organic carbon (TSOC). The bars are standard errors.

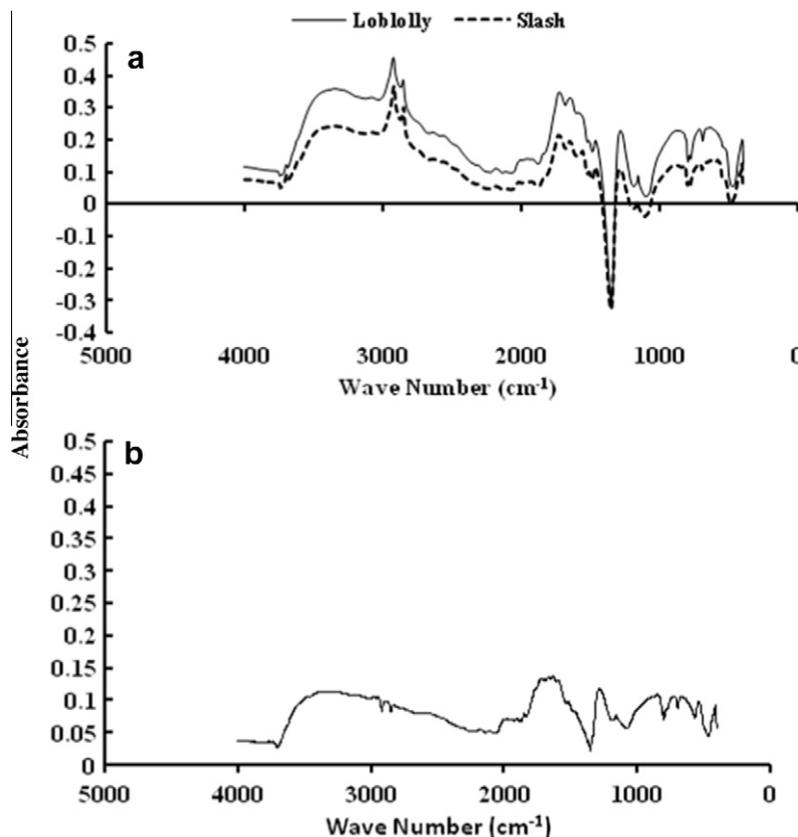
by the main effects of species and energy level without any significant interactions. The cumulative ASOCg and ASOC% increased with ADE as expected (Fig. 2). The ASOCg in soil under loblolly pine was higher than under slash pine (Fig. 2a). The difference between species was most evident above  $60 \text{ J mL}^{-1}$ . Averaged for all energy levels, ASOCg was 48% greater for loblolly than slash pine surface soil. At the highest dispersion energy, loblolly ASOCg was 62% higher than slash pine ASOCg (Fig. 2a). The ASOC% is a normalized look at aggregate C (Fig. 2b) which shows that a significantly greater proportion of slash pine C (12% greater) was incorporated into aggregates.



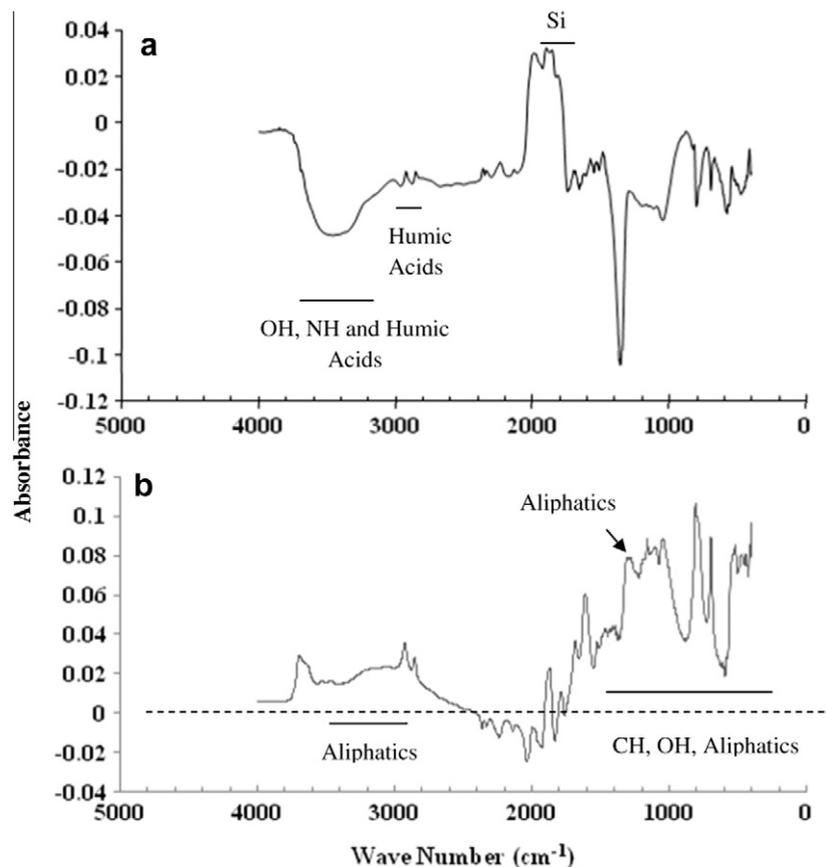
**Fig. 4.** The amount of dissolved organic carbon (DOC) released from the  $2 \text{ mm}$  to  $53 \text{ }\mu\text{m}$  soil size fraction upon sonication at  $0, 58$  and  $153 \text{ J mL}^{-1}$  dispersive energy levels. The bars are standard errors.

### 3.3. Objective 3 – ASOC mineralization

Soil aggregate strength did not affect carbon mineralization in any of the treatments (main effect of energy level  $p = 0.78$ ), showing that aggregation in these sandy soils did not protect ASOC from decomposition. However, there was a significant influence of pine species on the cumulative mineralization of TSOC over the 29 week



**Fig. 5.** Diffuse reflectance infrared Fourier-transform spectra after 29 weeks of mineralization showing (a) the surface mineral soil horizon under slash and loblolly pine, and (b) the difference in spectra of loblolly pine soil minus slash pine soil.



**Fig. 6.** Diffuse reflectance infrared Fourier-transform spectra where spectra measured on soil material at week 29 of the mineralization was subtracted from week 1 of mineralization (using ash subtracted spectra for soils influenced by (a) loblolly pine and (b) slash pine. Absorbances above 0.0 indicate an increase of week 1 over week 29 and absorbances below 0.0 indicate a decrease of week 1 over week 29.

time interval ( $p < 0.01$ ). The slash pine soils showed a 27% higher mineralization rate over the soils under loblolly pine ( $96 \text{ vs. } 75 \text{ mg g}^{-1} \text{ TSOC}$ ; Fig. 3).

As the ADE increased, loblolly pine soils released more DOC than did those under slash pine (Fig. 4). At the highest ADE, loblolly pine soil released an average of 48% more DOC. After 12 weeks there was no significant effect of the dispersion energy or species on DOC specific mineralization rate ( $p = 0.93$  and  $0.69$ ; respectively). Mean DOC mineralization after 12 weeks, across all treatments and species, was  $0.019 \text{ mg C g}^{-1} \text{ TSOC}$ .

#### 3.4. Objective 4 – DRIFTS spectra

The DRIFTS spectra indicated that functional group assemblages in the soil were influenced by the ecosystem's vegetation (Fig. 5). Loblolly and slash pine ash-subtracted spectra are presented as individual spectra (Fig. 5a). Overall the higher absorbance in the loblolly soils was consistent with the higher organic C in those soils. The comparison between slash pine and loblolly pine soils is presented as a single spectrum where slash pine was subtracted from loblolly pine (Fig. 5b). When presented in this fashion, the downward trends indicated a relative decrease in loblolly compared to slash; and an upward trend indicated a relative increase in loblolly pine soils relative to slash pine soils. Slash pine soil had more aliphatic C–H groups ( $2900\text{--}3000 \text{ cm}^{-1}$ ; Reeves and Smith, 2009; Madari et al., 2005). Loblolly pine soils had more aromatic carboxylic acids ( $1600\text{--}1700 \text{ cm}^{-1}$ ; three peaks between  $650$  and  $850 \text{ cm}^{-1}$ ; Reeves, III et al., 2006; Celi et al., 1997).

The soil under each species was influenced differently by mineralization as evidenced by subtracting spectra for samples after 29 weeks of mineralization from spectra collected after 1 week of

mineralization (Fig. 6). Loblolly pine ecosystems (Fig. 6a) showed a decrease in absorbance between  $3000$  and  $3600 \text{ cm}^{-1}$ . This is a general region for humic C–H. The triplet band at  $1800\text{--}2000 \text{ cm}^{-1}$  is due to an increase in silica over time as SOC decreases. Finally, an accumulation of aromatics occurred with the degradation of the humic substances. Subtraction spectra for slash pine soils (Fig. 6b) had an increase in aliphatic C as indicated by the bands around  $2900\text{--}3000 \text{ cm}^{-1}$ . Large peaks at  $3000\text{--}3500 \text{ cm}^{-1}$  (peaks  $3531$ ,  $3460$ ,  $3170$ , and  $3054$ ) and a specific peak at  $1295 \text{ cm}^{-1}$  were attributed to aliphatic functional groups. The triplet band at  $1800\text{--}2000 \text{ cm}^{-1}$  for silica due to SOC loss was evident for the slash pine soils as well. Overall, there was an accumulation of aliphatic materials in slash pine soils over time of mineralization; while loblolly-pine-affected soils had an accumulation of humic and aromatic soil material.

#### 4. Discussion

Aggregate dispersion curves have been used to qualitatively and quantitatively describe ASOC. Microscopic evidence verified that sonication was dispersing soil aggregates, therefore the method was deemed useful for the purpose for which it was employed. Surface soil horizon aggregates were bound by mycorrhizal hyphae, fine roots, and microbial and fungal debris, consistent with observations of Kay (1997) and Degens et al. (1996) in sandy soils. The reason for higher aggregate stability in the  $150\text{--}250 \text{ }\mu\text{m}$  size fraction, and the higher dispersion energy required for total aggregate dispersion, should be explored both for mechanism of stability and potential for C sequestration.

The major findings of this study were that aggregates did not protect ASOC from mineralization in these very sandy soils.

Loblolly pine surface mineral horizons accumulated more TSOC than slash pine soil horizons; while slash pine soils had higher specific mineralization rates than loblolly pine soils. This is partially explained by DRIFTS spectra that showed that soils under loblolly pine were more aromatic than those under slash pine – and became more aromatic as mineralization proceeded.

Loblolly pine is recognized as a species that has a greater leaf area index and greater annual leaf litter fall than slash pine (Colbert et al., 1990; Jokela and Martin, 2000; Will et al., 2001; Xiao et al., 2003; Burkes et al., 2003). It has also been described as supporting a greater cohort of fine roots (Burkes et al., 2003; Nowak and Friend, 2006) and more mass in its forest floor (Polglase et al., 1992), particularly in plantation environments. Accumulation of TSOC is a function of rate of C input vs. mineralization. Therefore, it is not surprising that the TSOC is greater for loblolly than slash pine.

The lack of a significant effect of aggregation on the rate of mineralization was supported by the work of others on sandy soils. Our findings support the contention that ASOC mineralization was more related to the stability of the SOC than to the physical protection of aggregation (Christensen, 1985, 1987; Buyanovsky et al., 1994). However, this statement only applies to very sandy soils. Our results conflict with the concept that formation of macroaggregates facilitates the accumulation of SOC and, given favorable conditions, physical protection is promoted by formation of stable aggregates (Jastrow, 1996). The very low clay content of Florida Spodosol surface horizons precludes formation of clay-dominated aggregates that could physically occlude and protect C.

The mineralization rate difference found between loblolly and slash pine provides more evidence as to why TSOC levels are higher in loblolly pine surface soils. The soil under slash pine had higher specific mineralization rates. The higher C inputs to the soil under loblolly pine and the lower mineralization rates of SOC under loblolly pine resulted in higher TSOC in these sandy soils. This is the first report showing that mineral soil TSOC mineralization is a function of southern pine species.

However, it should be noted that all mineralization rates were measured under laboratory conditions and at near optimum water potential. These are not dynamic field conditions. We are unable to determine from these data if our results would be different if the soils were mineralized under differential water regimes that better reflected average or dynamic field water potentials. Differential mineralization due to inherently different moisture regimes based on ecosystem water use, and due to differential understory contributions to soil detritus could form the basis of an alternative hypothesis. However, we think that this, as an alternative explanation of increased TSOC under loblolly systems, is unlikely. When the water table is within approximately 65–70 cm of the soil surface, the surface water potential is controlled by the water table, not the vegetation (Phillips et al., 1989). With water tables below that depth, surface water potential drops rapidly. Since loblolly pine carries a higher leaf area, evapotranspiration would be expected to be higher causing more rapid site drying, reducing surface horizon SOC mineralization, and increasing TSOC. We are not aware of any studies contrasting water regimes of slash and loblolly pine ecosystems on these soils, so at this time the alternative hypothesis is speculative, but may be worthy of future study to determine how differential moisture regimes of these ecosystems may control TSOC accumulation.

Finally, the DRIFTS spectra explained why loblolly pine soils have lower specific mineralization rates. That is due to more aliphatic C–H present in slash pine soils, which is most likely related to waxes or methyl groups. These groups are more bioavailable than the larger amount of aromatic carboxylics present in loblolly pine soils. Likewise, decomposition of TSOC resulted in more

aromatic functional groups accumulating in the loblolly pine soils; continuing the trend of lower mineralization rates.

There was a clear difference in the SOC quality between sites dominated by different overstories. The quality of needles and roots of all ecosystem vegetation components has not been widely studied and these data imply that more detailed work on the quality of organic C inputs; i.e. nutrient concentrations and functional group characterization of roots, leaves, branches; will be necessary in order to mechanistically quantify C cycling differences within soils influenced by these different ecosystems. It must be remembered that the ecosystem is composed of more than the tree component and the role of the understory plants in these ecosystems should not be dismissed. While this study did only a cursory observation of understory characteristics, these results are a combined effect of all site vegetation. To fully understand the influence of loblolly and pine ecosystems on soil carbon, it will be useful in the future to consider the range of chemical characteristics and levels of OC input from all ecosystem plant components.

Due to their dominance in the Lower Coastal Plain of the US, pine ecosystems play an important role in the conversion of atmospheric CO<sub>2</sub> into the TSOC pool. Soil aggregation should not be considered a mechanism to protect SOC in these very sandy soils when modeling soil C dynamics, even though slash pine systems show a slightly greater capacity to develop aggregates. The tree species to grow on these sandy soils is based on management objectives. However, if one of the reasons is to sequester TSOC, the chemical quality of C inputs and the quantity of those inputs favor the use of loblolly pine plantations.

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