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The influence of microbial communities, management, and soil texture on soil organic matter chemistry

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ABSTRACT

Soil organic matter dynamics following land-use change remain difficult to predict because of the complex biological, physical, and chemical mechanisms that control C turnover. We examined twelve sites, representing four broad land-use types (cultivated agriculture, pine forest, hardwood forest, and pasture), in the South Carolina Piedmont to determine whether variation in organic matter chemistry was linked to management, soil edaphic properties, microbial communities, or labile C. Organic matter chemistry was determined before and after a 232-d incubation using pyrolysis gas chromatography/mass spectroscopy and microbial community properties were determined prior to incubation by measuring extracellular enzyme activities, fungal:bacterial ratios by quantitative polymerase chain reaction (PCR), and microbial biomass. There was considerable variation in soil organic matter chemistry among the 12 sites but this could not be attributed to broad differences in land use, per se, likely because of the variation in edaphic soil properties and specific management practices within the individual land use categories. The relative abundance of N-containing compounds was correlated with the size of the labile C pool ($r=0.65$). Further, the three most abundant N-containing pyrolysis products, pyridine, pyrrole, and indole, were also positively correlated with at least two enzymes and both pyridine and pyrrole were negatively correlated with fungal:bacterial ratios. In contrast, the relative abundances of lignin derivatives were often negatively correlated with enzyme activities but positively correlated with fungal:bacterial ratios. Post-incubation, silt plus clay content was negatively correlated with lignin derivatives ($r=-0.68$) and positively correlated with N-containing compounds ($r=0.69$). Our results suggest that broad land use categories are a poor predictor of soil organic matter chemistry when edaphic soil properties and specific management practices vary. However, enzyme activities, fungal:bacterial ratios, and soil texture correlate with soil organic matter chemistry across a range of ecosystems, suggesting that interactions between microbial communities and soil organic matter chemistry are important controls on soil C dynamics across landscapes.

1. Introduction

Soil organic matter (SOM) chemistry represents the dynamic interplay between heterogeneous plant inputs, soil organisms, and physiochemical stabilization processes (Kögel-Knabner et al., 2006; von Lützow et al., 2008). For this reason, it is difficult to predict how soil carbon chemistry will change across space and time. Some studies have observed that SOM is consistent across sites (Guggenberger et al., 1995; Mahieu et al., 1999; Mendham et al., 2002; Dieckow et al., 2005) and that changes in vegetation or in disturbance intensity may have little if any effect on SOM chemistry. Gleixner et al. (2002), for example, used pyrolysis GC/MS to show that maize and wheat cropping systems at Boigneville in northern France were similar to each other and to soils from other regions and ecosystems.

However, other studies have found changes in land use can result in notable differences in SOM chemistry in both agricultural and forest systems (Helfrich et al., 2006; Magrini et al., 2007; Ussiri and Johnson, 2007; Marin-Spiotta et al., 2008). For example, Quideau et al. (2001) found that litter chemistry was linked to differences in SOM chemistry and questioned the idea that soil properties and microbial processing leads to uniformity in SOM structure. Grandy et al. (2007) showed in mountain ecosystems that lignin and polysaccharide abundance are influenced by both site elevation and geochemical soil properties. Additional studies have shown that SOM chemistry is influenced by plant communities (Nierop et al., 2001a,b; Filley et al., 2008a), earthworms (Filley et al., 2008b), tillage (Sleutel et al., 2007), fertilizer use (Wang et al., 2004; Marinari et al., 2007), and other management or environmental factors (Preston et al., 2002; Ganjegunte et al., 2005),

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including clay mineralogy (Buurman et al., 2005). These contrasting results highlight the need for studies that characterize SOM chemistry across a greater range of sites in order to build a predictive understanding of SOM dynamics.

In particular, the characterization of SOM chemistry across a range of soil types, coupled with analyses of soil organisms, may help us understand how SOM chemistry interacts with soil biological communities to control C stabilization and other soil functions. For example, Leinweber et al. (2008) have shown that during laboratory incubations xylanase activity was closely related to the ratio of xylan to xylose and Grandy et al. (2007) found strong correlations between enzymes and SOM composition, particularly the chemistry of the light fraction SOM, in mountain ecosystems. Grandy et al. (in press) and Gallo et al. (2005) recently demonstrated that simulated N enrichment in forest ecosystems can alter oxidases in ways that translate directly into changes in the abundance of carbohydrates and lignin derivatives.

Other than enzyme–SOM interactions, microbial communities may also influence SOM chemistry since distinct microbial taxa may differ in their rates of C metabolism and the pools of C metabolized (Cavigelli et al., 1995; Balser et al., 2005). Further, the chemical composition of microbial biomass C can vary depending on microbial community composition (Cavigelli et al., 1995; Kögel-Knabner, 2002; Balser et al., 2005) and, although microbial biomass represents <5% of SOM at any point in time (Cleveland and Liptzin 2007), the overall contribution of microbially-derived compounds to SOM is potentially much greater (Simpson et al., 2007).

There remains considerable debate over the degree to which SOM chemistry is linked to its stability and long-term storage in soils. Leinweber et al. (2008) found that the thermal properties and chemistry of SOM were related to their breakdown during incubation. Gleixner et al. (2002), however, proposed that the chemistry of stable SOM varied across sites, reflecting the potential for a range of mechanisms other than SOM chemistry to control its stability. Laboratory incubations of soil provide a controlled environment for understanding the mechanisms underlying changes in SOM chemistry during decomposition and their relationship to biological processes and C storage. Specifically, long-term laboratory incubations provide insights into the potential for changes in SOM during decomposition because they: 1) remove environmental variation that can contribute to variation in microbial processes and SOM chemistry; and 2) reduce the likelihood that exogenous C inputs from litter deposition or root exudation will mask changes in SOM chemistry; and 3) accelerate SOM decomposition. Further, relationships between SOM chemistry and soil respiration rates can also provide information about which SOM constituents are selectively preserved or oxidized during decomposition (Wickland and Neff, 2008; Leinweber et al., 2008).

In agricultural landscapes, land use intensity usually reflects the potential productivity of a site and soils under different land-uses typically have distinct edaphic properties. Our overall goal was to examine how edaphic soil properties and microbial communities influence SOM chemistry under management and soil conditions typical for the South Carolina Piedmont region. Our specific objectives were to determine: 1) variation in SOM chemistry across a range of soil types with variable management and soil texture; 2) the relationships between SOM chemistry and biological processes including microbial enzyme activities, microbial biomass, and fungal:bacterial ratios; and 3) whether SOM loss during long-term incubation is related primarily to total C, C chemistry, or biological processes and whether these losses are evenly distributed across SOM chemical groups.

2. Materials and methods

2.1. Site description

Our experimental sites, described in detail by Lauber et al. (2008), were located in or adjacent to the Calhoun Experimental Forest (CEF). CEF is managed by the U.S. Department of Agriculture and is located in the Piedmont region (approximately 34.5°N, 82°W) of northwestern South Carolina, U.S. (Gaudinski et al., 2001, Callaham et al., 2006). We examined four different types of land use common in this area of the U.S. (Callaham et al., 2006): annual-row crop agriculture with cultivation, pasture, pine plantation, and oak-hickory hardwood forest. Soils at these sites developed under humid conditions, are highly weathered, and classified as fine, kaolinitic, thermic Typic Kanhapludults of the Appling, Cecil and Madison Series (Callaham et al., 2006). Our goal was to understand SOM dynamics under management and soil conditions typical for this region. For this reason, sites classified into the same broad land-use category may not necessarily have the same edaphic characteristics or specific management practices.

The annual cropping systems, managed by the South Carolina Dept. of Natural Resources, are cultivated and rotate between corn, millet, wheat, sorghum, sunflowers and fallow (Callaham et al., 2006). Pasture sites are grazed, untilled grasslands dominated by rye grass. The cultivated and pasture sites were established more than 40 years ago (Callaham et al., 2006). Two of the pine forest sites (one and three) consist of loblolly pine (*Pinus taeda*) with oak and hickory species in the understory (*Quercus* spp., *Carya* spp.); the other pine forest is a loblolly pine monoculture. Pine plots 1 and 3 are approximately 50 years old, while plot 2 is 10 years in age (Callaham et al., 2006). The hardwood sites are mature mixed oak-hickory stands that have not been tilled. One of the hardwood sites (two) is grazed by cattle and has little understory vegetation.

2.2. Soil collection and edaphic soil properties

In September 2006 we used a stratified random sampling approach to collect 10 soil cores (8 cm diameter) from each of the 12 sites. At each site, we established a 10 × 10 m sampling area and then randomly sampled within this plot. We sampled the surface mineral horizon from 0 to 7.5 cm depth. These 10 cores per plot were combined to minimize within plot spatial variation, sieved (4 mm), homogenized, and stored at 5 °C for less than 10 days prior to conducting the biological analyses (see below). Soil pH was determined in water (1:1 volumetric ratio of water-to-soil) using a benchtop pH meter. Silt and clay contents were measured using a simplified version of the hydrometer method as described by Gee and Orr (2002).

2.3. Enzyme activities

We estimated the activity of six enzymes (β-1-4-glucosidase (BG), L-leucine-aminopeptidase (LAP), β-1-4-*N*-acetylglucosaminidase (NAG), phenol oxidase (PHEN) and peroxidase (PER)) using previously published protocols (Saiya-Cork et al., 2002; Stursova et al., 2008). Soil slurries were prepared by adding 1 g soil to 125 ml sodium acetate buffer (50 mM, pH 5.0) and shaken by hand to homogenize. Aliquots (200 µl) were dispensed from continuously stirred samples into 16 replicate wells per assay on 96-well microplates. Wells for reference standards, sample quenching or absorbance and negative control were also prepared. Wells for fluorescent assays received 50 µl of 200 µM of the appropriate methyllumbelliferyl (MUB) linked substrate. Reference standard and sample quenching wells received 50 µl of 10 µM 4-methylumbelliferone or 7-amino-4-methyl coumarin (LAP only). The MUB fluorescence was measured after the addition of 10 µl NaOH (0.5 M) using the 360 nm excitation and 460 nm filter pair on a BioTek Synergy HT microplate reader.

The activity of PHEN and PER was determined spectrophotometrically from the oxidation of L-3,4-dihydroxyphenylalanine (L-DOPA). Fifty microliter aliquots of 10 mM L-DOPA were added to the negative control and assay wells. Hydrogen peroxide (10 µl, 0.3%) was also added to each well on the PER assay plates. The absorbance was monitored at 450 nm on a BioTek Synergy HT microplate reader. All

Table 1
Soil C distribution, chemistry, and pH associated with different land uses.

	pH	Silt + clay	Total C	Total N	C/N	Labile C	POM C	POM N	S + C–C	S + C–N
		%	mg g^{-1}	mg g^{-1}	–	mg g^{-1}	mg g^{-1}	mg g^{-1}	mg g^{-1}	mg g^{-1}
Cultivated	5.71	38.76a	12.34ab	0.84a	14.68	0.66	4.59	0.20	7.75a	0.64a
	(0.65)	(2.87)	(1.66)	(0.08)	(1.18)	(0.16)	(0.74)	(0.02)	(0.99)	(0.06)
Pasture	4.23	20.95b	9.88b	0.70a	14.16	0.76	6.08	0.33	3.75b	0.36b
	(0.18)	(4.16)	(0.70)	(0.04)	(0.41)	(0.08)	(0.79)	(0.05)	(0.08)	(0.01)
Hardwood	4.39	30.09ab	18.30a	0.83a	19.00	1.29	9.91	0.33	8.33a	0.50ab
	(0.48)	(3.18)	(3.80)	(0.04)	(0.69)	(0.43)	(2.42)	(0.07)	(1.00)	(0.03)
Pine	5.51	17.74b	8.64b	0.39b	23.92	0.64	4.79	0.16	3.85b	0.23b
	(0.35)	(3.12)	(0.44)	(0.08)	(4.96)	(0.06)	(0.21)	(0.04)	(0.24)	(0.04)
ANOVA Ecosystem	0.727	0.009	0.031	0.003	0.120	0.242	0.072	0.074	0.003	0.000

Abbreviations: POM = particulate organic matter >53 µm; S + C = silt plus clay associated C or N.
Different letters indicate statistically different ecosystem means within a variable determined using Tukey's Test.
Numbers in parentheses below means are standard errors.

plates were incubated in the dark at 22 °C for the duration of the experiment. Activities were corrected for soil moisture and expressed as nmol h^{-1} g^{-1} soil. Enzyme commission (EC) numbers and substrates for each enzyme are as follows: BG, 3.2.1.21, 4-MUB-β-D-glucoside; LAP, 3.4.11.1, L-leucine-7-amino-methylcoumarin; NAG, 3.2.1.14, 4-MUB-*N*-acetyl-β-D-glucosaminide; AP, 3.1.3.2, 4-MUB-phosphate phenol oxidase; PHEN, 1.10.32, L-3,4-dihydroxyphenylalanine; and PER, 1.11.17, L-3,4-dihydroxyphenylalanine.

2.4. Fungal:bacterial ratios

Immediately after homogenization of the 10 soil cores per plot, DNA was extracted from the homogenized samples using the MoBio PowerSoil DNA extraction kit as described in Lauber et al. (2008). The relative abundances of bacteria and fungi were determined using methods described in detail in Lauber et al. (2008) according to the quantitative PCR (qPCR) approach described in Fierer et al. (2007). All qPCR reactions were run in quadruplicate with pooled DNA sample from each plot.

2.5. Soil C pools

To estimate the size of the labile carbon pool we used a static incubation procedure (Fierer et al., 2003). We added an equivalent of 6 g dry weight soil to 50 ml centrifuge tubes. The soil was adjusted to 65% water holding capacity and maintained at this level throughout the incubation. All soils were incubated at 20 °C and 100% humidity for 232 days. During this period, carbon mineralization rates were periodically determined by sealing each tube with an airtight cap equipped with a septum. Tubes were then flushed with CO_2-free air and incubated at 20 °C for 24 h. After this incubation period gas samples were taken via syringe and analyzed using an infrared gas analyzer (IRGA) (LI 7000; Li-Cor Inc., Lincoln, USA). The labile carbon pool was estimated using the simplified two-order model described by Dijkstra et al. (2005). This model assumes that the mineralization of recalcitrant C will remain relatively constant across the course of the incubation but that the contribution of the labile C will decline across time. This model effectively estimates the cumulative amount of C mineralized (minus the contribution of recalcitrant C) up until C-mineralization reaches a steady state.

Particulate organic matter (POM) was determined by dispersing the soils in sodium hexametaphosphate for a minimum of 18 h and then pouring the suspension through a 53 µm sieve using the methods outlined in Paul et al. (2001). The collected material that was >53 µm was classified as POM and the material smaller than this was classified as silt + clay C (or mineral-associated fractions). Carbon and N concentrations of whole soils, POM, and silt + clay C were determined using an NA1500 CHN Analyzer (Carlo Erba Strumentazione, Milan, Italy). Soil pH was determined in water (1:1 volumetric ratio of water-to-soil) using a benchtop pH meter.

Microbial biomass C and N were determined using a modified form of the chloroform fumigation–extraction described in Fierer and Schimel (2003). Briefly, we dispersed the soils in 40 ml of 0.5 M K_2SO_4 and fumigated a subset of samples by adding 1 ml of EtOH-free $CHCl_3$ in order to extract microbial biomass C and N. These were then shaken for 3 h at 150 RPM after which the samples were gravity filtered and all samples were aerated vigorously for up to 1 h in order to remove any $CHCl_3$ from the subset of fumigated samples. All samples were then stored at −20 °C until colorimetric (N) and total organic C analysis. No correction factor was used to adjust microbial biomass estimates.

2.6. Organic matter chemistry

We used Curie-point pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) to determine the molecular chemistry of SOM in whole soil samples (Hempfling and Schulten, 1990; White et al., 2004; Kaal et al., 2007; Adani et al., 2007) before and after the 232-d incubation using methods described in detail elsewhere (Neff et al., 2005; Grandy et al., 2007). Samples were pyrolyzed using a Curie-Point pyrolyzer (Pyromat, Brechbühler Scientific Analytical Solutions, Houston, USA) at 590 °C in pyrofoils (Pyrofoil F590, Japan Analytical Company, Tokyo, Japan). Following pyrolysis, compounds were transferred online to a gas chromatograph (ThermoQuest Trace GC, Thermo Finnigan, San Jose, USA) with an interface temperature of 250 °C and a split injection ratio of 50:1 (He flow rate 1.0 ml min^{-1}). Compounds were separated on a BPX 5 column (60 m × 0.25 mm, film thickness 0.25 µm) using a temperature program of 40 °C for 5 min, 5 °C min^{-1} to 270 °C followed by a jump (30 °C min^{-1}) to a final temperature of 300 °C. The GC was connected to a Thermo Polaris-Q ion-trap mass spectrometer (Polaris Q, Thermo Finnigan, San Jose, USA) operated at 70 eV in the EI mode. The transfer line temperature was 270 °C and the source temperature was held at 200 °C. Each run lasted 62 min and the mass/charge scan range was 35–300.

Peaks were compared to reference spectra after deconvolution and extraction using AMDIS v. 2.64, the National Institute of Standards and Technology mass spectral libraries, and published literature (Saiz-Jimenez, 1994; Stankiewicz et al., 1997; Nierop et al., 2001a,b; de Alcântara et al., 2004; Buurman et al., 2005; Wickland and Neff, 2008). Our results are expressed as relative compound abundance by normalizing results to the largest peak measured in the chromatogram. These data do not provide insight into the absolute abundance of compounds across samples, and is thus not quantitative, but does provide a broad molecular profile of the organic composition of soils. We identified the dominant 26 compounds as those representing, on average, >1% of total signal either before or after the 232 day incubation. In addition to identifying the dominant moieties, we

Table 2
Soil enzyme activity, fungal/bacterial ratios, and microbial biomass across sites.

	NAG	BG	LAP	PHOS	PER	PHEN	Fungi:Bac	MBC	MBN
	nmol h^{-1} g^{-1}	nmol h^{-1} g^{-1}	nmol h^{-1} g^{-1}	nmol h^{-1} g^{-1}	nmol h^{-1} g^{-1}	nmol h^{-1} g^{-1}		μg g^{-1}	μg g^{-1}
Cultivated	49.78b	95.64	3.05ab	264.31	734.17	381.49	0.03b	51.74ab	7.65b
	(6.62)	(13.56)	(0.40)	(79.58)	(195.04)	(80.48)	(0.01)	(1.23)	(0.28)
Pasture	49.69b	81.08	3.22ab	242.46	612.73	165.51	0.03b	20.20b	2.95bc
	(14.63)	(17.30)	(0.83)	(41.09)	(72.18)	(84.47)	(0.004)	(2.27)	(0.92)
Hardwood	100.31a	101.02	3.54a	331.47	599.17	263.25	0.05ab	92.03a	14.87a
	(8.02)	(9.11)	(1.00)	(24.37)	(118.71)	(177.95)	(0.008)	(17.42)	(1.98)
Pine	41.87b	44.54	0.39b	175.82	543.60	51.48	0.08a	35.47b	1.61c
	(8.82)	(14.82)	(0.19)	(20.15)	(47.83)	(46.64)	(0.01)	(4.50)	(0.74)
ANOVA ecosystem	0.012	0.079	0.040	0.221	0.736	0.251	0.026	0.003	0.002

Abbreviations: NAG (b-1,4-N-acetylglucosaminidase); BG (b-1,4-glucosidase); LAP (L-leucine aminopeptidase); PHOS (phosphatase); PER (peroxidase); PHEN (phenol oxidase); Fungi:Bac (fungal/bacterial ratios); MBC and MBN (microbial biomass C and N, respectively).
Different letters indicate statistically different ecosystem means within a variable determined using Tukey's Test.
Numbers in parentheses below means are standard errors.

grouped all compounds into five chemical classes based on their origin: polysaccharides, lignin derivatives, N-bearing compounds, lipids, and unknown compounds. Compounds classified as unknown were either ones that could not be identified or compounds that could not be definitively grouped into any of the above categories.

2.7. Statistical analyses

Differences in soil biological and chemical properties among land-use types were analyzed using analysis of variance (ANOVA, $n=3$). Where there were significant differences ($p<0.05$), individual ecosystem means were separated using a Tukey test. We additionally used principal components analysis to look at variation in SOM chemistry among individual sites because of the variation in management practices within broad land-use categories. Correlation analyses were used to explore the relationships between soil biological and chemical characteristics, and principal component analysis was used to develop a linear combination of the combined enzyme activities which could then be correlated with soil chemical properties. All statistical analyses were done using Statistica, Version 8 (StatSoft, Tulsa, OK, USA).

3. Results

There were no differences in pH among different land uses but there were significant differences in soil texture (Table 1). The cultivated sites had significantly more silt plus clay content than the pasture or pine forests. Total C concentration was greater in the hardwood ecosystems than the pasture or pine forests but not statistically different from that in the cultivated sites. Total soil N was lower in the pine forest than other ecosystems. Silt + clay C was lower in the pine forest and pasture ecosystems than the cultivated or hardwood

Table 3
The relative abundance of the most dominant compounds before and after a 232 incubation.

Compound	Source[†]	Preincubation[‡][§]	Significant correlations	Post-inc	Post-incubation mean seperation[§]
4-Vinylguaiacol	Lg	7.77 (0.97)	0	6.96 (1.06)	
4-Acetylguaiacol	Lg	3.95 (1.03)	**lap(−0.67)**, f/b(0.69)	1.52 (0.39)	
Guaiacol	Lg	3.62 (0.79)	**bg(−0.72)**, **lap(−0.73)**, f/b(0.58)	2.52 (0.41)	cult^{b}, grass^{ab}, hard^{a}, pine^{ab}
4-Formylguaiacol	Lg	2.47 (0.48)	0	1.32 (0.31)	cult^{c}, grass^{b}, hard^{b}, pine^{a}
4-Propenylguaiacol	Lg	1.77 (0.41)	mc(0.66)	1.3 (0.31)	
4-Methylguaiacol	Lg	1.34 (0.27)	0	1.3 (0.39)	
4-Propan-2-one-guaiacol	Lg	1.11 (0.32)	f/b(0.73)	0.33 (0.07)	cult^{b}, grass^{ab}, hard^{ab}, pine^{a}
Acetophenone	Lg	0.43 (0.10)	bg(0.82), lap(0.72), per(0.69), **f/b(−0.63)**	1.08 (0.17)	
Pyridine	N	1.40 (0.21)	bg(0.64), phen(0.60), **f/b(−0.58)**	1.41 (0.22)	
Pyrrole	N	1.39 (0.26)	bg(0.67), per(0.68), **f/b(−0.59)**	1.55 (0.32)	
Indole	N	1.26 (0.28)	nag(0.73), bg(0.61), lap(0.81), phos(0.70)	0.74 (0.17)	
Levoglucosenone	Ps	4.37 (1.29)	**bg(−0.63), phos(−0.68)**	4.02 (1.13)	cult^{b}, grass^{b}, hard^{b}, pine^{a}
Furfural	Ps	15.67 (1.79)	**phos(−0.70)**	19.17 (2.31)	
3-methyl-furan	Ps	1.43 (0.23)	bg(0.61), lap(0.65)	1.96 (0.55)	
2(5H)-Furanone	Ps	1.32 (0.34)	0	0.92 (0.27)	
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	Ps	1.20 (0.18)	0	1.07 (0.18)	
2-Acetylfuran	Ps	0.89 (0.13)	0	1.13 (0.19)	cult^{a}, grass^{b}, hard^{b}, pine^{b}
3-Furaldehyde	Ps	0.81 (0.15)	lap(0.59)	1.71 (0.37)	
2-Methylbutanal	Ps	0.80 (0.2)	0	1.03 (0.23)	cult^{a}, grass^{b}, hard^{b}, pine^{b}
2,3-Dihydro benzofuran	Ud	6.15 (1.14)	0	5.6 (1.09)	
Phenol	Ud	4.39 (0.71)	0	3.56 (0.88)	
Toluene	Ud	3.49 (0.5)	0	2.73 (0.52)	cult^{ab}, grassa^{b}, hard^{a}, pine^{b}
4-methyl-phenol	Ud	2.51 (0.44)	0	2.53 (0.49)	
3,4-dimethyl-phenol	Ud	1.61 (0.34)	bg	1.49 (0.24)	
Styrene	Ud	1.18 (0.17)	0	1.07 (0.23)	
Unknown	Ud	1.03 (0.22)	bg(0.72), lap(0.71), phen(0.63), per(0.74)	1.23 (0.33)	
		%		%	

[†] Source: Lg (lignin); N (N-bearing); Ps (polysaccharide); Ud (Undetermined).

[‡] Prior to incubation there were no significant differences in relative compound abundance between land uses. After incubation seven of the compounds varied by land use and mean separation was determined using a Tukey's Test ($p<0.05$).

[§] Significant correlations (r, $p<0.05$) are shown between the relative abundance of individual compounds prior to incubation and biological processes at the same sampling date. Abbreviations: nag (b-1,4-N-acetylglucosaminidase); bg (b-1,4-glucosidase); lap (L-leucine aminopeptidase); phos (phosphatase); phen (phenol oxidase); mc (microbial biomas C); per (peroxidase); f/b (fungal/bacterial ratios). Negative relationships are indicated in bold.

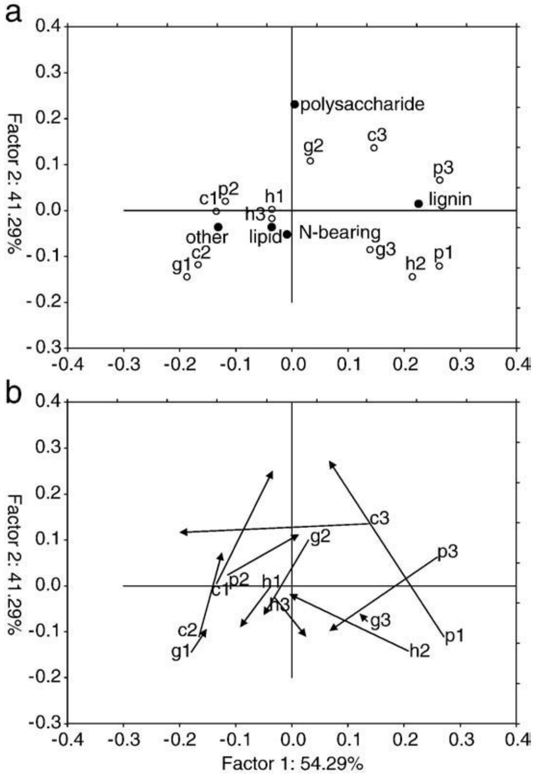

Fig. 1. Principal components analysis of the SOM chemistry among individual sites showing the contribution of chemical classes to each axis (a) and changes in SOM chemistry with incubation (b). Circles with abbreviations indicate SOM chemistry prior to incubation with arrows indicating SOM chemistry after incubation. Abbreviations: c1–c3 (cultivated sites one through three); g1–g3 (grassland pasture sites one through three); h1–h3 (hardwood forest sites one through three); p1–p3 (pine forest sites one through three).

treatments and silt + clay N was higher in the cultivated sites than in the pasture or pine forest ecosystems (Table 1).

There was a significant ($p<0.05$) land use effect on the activities of certain extracellular enzymes (NAG and LAP), fungal:bacterial ratios (which are discussed in greater detail in Lauber et al., 2008), and microbial biomass C and N (Table 2). The hardwood forest plots generally had the highest microbial biomass concentrations and enzyme activities (Table 2). The pine and hardwood forests had the highest fungal/bacterial ratios (Table 2).

We identified a total of 143 compounds (19 lignin derivatives, 22 lipids, 30 N-bearing compounds, 36 polysaccharides, and 36 compounds of unknown origin). The 26 most abundant products of py-GC/MS represented lignin derivatives (8 compounds), N-bearing compounds (3 compounds), polysaccharides (8 compounds), or other (7 compounds) based on their origin (Table 3). There was no difference among land uses in the relative abundance of these 26 compounds prior to incubation. After the 232-d incubation, the relative abundance of seven of these compounds did differ by land use (guaiacol, 4-propan-2-one-guaiacol, 4-formylguaiacol, levoglucosenone, 2-acetylfuran, 2-methylbutanal, and toluene). When all of the compounds identified using py-GC/MS were classified by their origin, there were considerable differences in SOM chemistry among individual sites and distinct changes in chemistry during incubation (Fig. 1). When these sites were grouped by land use there were no differences in SOM chemistry prior to incubation (Table 4). After incubation, there was about 3–6-fold greater lipid abundance in the hardwood sites compared to the other sites.

Prior to incubation, we observed a number of significant correlations between the relative abundances of our 26 most abundant compounds, enzyme activities, and fungal:bacterial ratios (Table 3). Twelve of the compounds were not correlated with enzymes or fungal:bacterial ratios. Non-significant (4-methylguaiacol, 4-vinylguaiacol, 4-formylguaiacol, and 4-propenylguaiacol) or negative (4-acetylguaiacol, guaiacol, 4-propenylguaiacol, and 4-propan-2-one-guaiacol) correlations were noted between our most abundant lignin derivatives and specific enzymes while fungal:bacterial ratios were positively correlated with three of the lignin derivatives (Table 3).

In contrast to lignin, the three most abundant N-containing compounds were all positively correlated with at least two enzymes: pyridine (BG, PHEN), pyrrole (BG, PER), and indole (NAG, BG, LAP, and PHOS). Both pyridine and pyrrole were also negatively correlated with fungal:bacterial ratios. Within the polysaccharides group, the abundance of specific compounds varied with measured enzyme activities. Four of the eight compounds were not correlated with biological processes. Furfural was negatively correlated with PHOS. Levoglucosenone was negatively correlated with BG and PHOS. 3-methyl-furan was positively correlated with BG and LAP, and 3-furaldehyde was positively correlated with LAP (Table 3).

4. Discussion

We studied soil biological processes and SOM chemistry among 12 distinct sites and found that the N content of SOM was strongly correlated with biological processes and that soil texture strongly predicted both the abundance of N containing compounds and lignin derivatives. When we grouped these twelve sites into discrete land use types, we were unable to detect management effects on SOM chemistry expressed as either the dominant individual moieties or as chemical groups. However, there was considerable variation in soil texture and even specific management protocols among sites within the individual land-use categories. This variation is expected, as soils are rarely managed identically and specific management practices typically reflect the potential productivity and limitations of a given site. Under these kinds of 'real-world' scenarios where soil management practices differ under highly variable soil conditions, relationships among SOM chemistry, biological processes, and

Table 4
Distribution of C by origin among sites.

	Pre-incubation					Post-incubation				
	Lignin	Lipid	N-bearing	Other	Poly	Lignin	Lipid	N-bearing	Other	Poly
Cultivated	17.13	1.45	12.05	37.31	32.06	6.92	2.20b	11.96	34.84	44.08
	(6.08)	(0.67)	(4.51)	(7.46)	(6.61)	(2.97)	(0.85)	(4.51)	(4.17)	(5.05)
Pasture	22.73	0.21	8.60	39.24	29.22	21.72	1.98b	7.70	42.37	26.22
	(7.03)	(0.13)	(1.76)	(7.98)	(6.20)	(6.36)	(0.99)	(2.33)	(4.13)	(1.06)
Hardwood	26.88	1.38	11.34	33.51	26.89	20.65	6.84a	9.63	38.40	24.48
	(8.32)	(0.51)	(2.98)	(1.53)	(3.39)	(3.08)	(0.87)	(2.58)	(1.74)	(2.76)
Pine	33.18	1.39	5.05	29.16	31.22	22.56	1.15b	4.27	31.10	40.91
	(11.27)	(0.60)	(1.73)	(4.93)	(9.32)	(3.73)	(0.60)	(1.73)	(4.93)	(9.32)
ANOVA ecosystem	0.606	0.668	0.443	0.700	0.907	0.094	0.005	0.174	0.285	0.078

Different letters indicate statistically different ecosystem means within a variable determined using Tukey's Test.
Numbers in parentheses below means are standard errors.

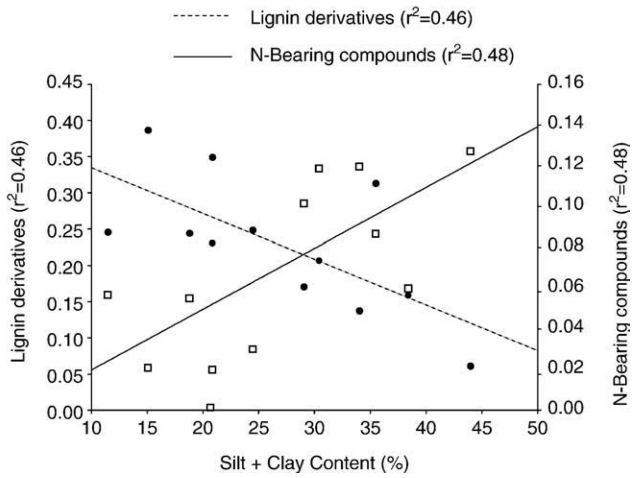

Fig. 2. Relationship between lignin derivatives and N-containing compounds (after incubation) and soil silt plus clay content.

edaphic soil properties can be strong and provide insights into the basic controls over soil biogeochemical processes across land-use types.

4.1. Labile carbon and SOM chemistry after incubation

The long-term incubations provided an opportunity to examine how soil biogeochemical properties interact to influence SOM chemistry over time under conditions favorable for decomposition and isolated from new C inputs. Although we were not able to detect any differences in SOM chemistry between land-use types prior to incubation, differences in total lipids and seven dominant pyrolysis products, including several polysaccharides and lignin derivatives, were detectable after incubation.

It has been hypothesized that while polysaccharides are not biochemically resistant to microbial attack, they may be abundant in soil because there is continuous production of microbial polysaccharides, which are incorporated into microaggregates and ultimately stabilized by organo-mineral interactions (Grandy and Neff, 2008; Kögel-Knabner et al., 2008). The protection of polysaccharides by soil minerals explains their increased relative abundance in intensively disturbed soil (Kiem and Kögel-Knabner, 2003) and their accumulation in clay fractions (Kiem and Kögel-Knabner, 2002; Grandy et al., 2007) and suggests that differences in polysaccharides should be especially apparent following long-term incubations under conditions favorable for decomposition. Indeed, we detected a trend towards differences in polysaccharide-derived pyrolysis products ($p<0.078$) between land use types and the average relative polysaccharide abundance in cultivated sites (44.08) was greater than that in pasture (26.22) or hardwood (24.48) sites. These results provide additional evidence suggesting that polysaccharide abundance will increase where disturbance and environmental conditions accelerate decomposition. However, the abundance of polysaccharide-derived pyrolysis products was similar in pine and cultivated sites, indicating that factors other than cultivation can also increase polysaccharide-derivatives.

Interestingly, we found that individual polysaccharide derivatives did not respond the same to land use after incubation, which may explain why the land use effect on total polysaccharides is not stronger. Land use influenced 2-methybutanal, 2-acetylfuran, and levoglucosenone following incubation but not the other polysaccharides. This, plus differences in correlations with enzymes (Table 3) and with compound classes suggests that there may be different sources of polysaccharides. We ran correlations between furfural and levoglucosenone and the compound classes before and after incubation (data not shown). Prior to incubation, furfural was related only to total polysaccharides. Prior to incubation levoglucosenone was negatively related to N (−0.84) and other compounds(−0.74). There also appeared to be a relationship with lignin (0.54) which was significant at $p<0.1$. After incubation, furfural was negatively related to the abundance of lipids (−0.57) and other compounds (−0.80), and levoglucosenone was negatively correlated with N-containing compounds (−0.82). These data are not conclusive but suggest the possibility that levoglucosenone was associated with SOM containing lower N contents and higher lignin contents (i.e. less decomposed) than furfural.

The 3–6-fold greater lipid abundance in the hardwood sites after incubation may be explained by intense degradation producing enrichment of the resistant aliphatic material, particularly of root-derived SOM that is fairly resistant to microbial decay (Rasse et al., 2005; Lorenz et al., 2007). Root derived aliphatic compounds are biochemically resistant to microbial decay and may accumulate where root inputs are high. The root inputs in the hardwood forest systems were likely higher than those in the agricultural systems and recent research has shown that shifts from herbaceous to woody plant communities can stimulate SOM accumulation in root-derived aliphatic pools (Filley et al., 2008a).

The observed correlations between soil texture and lignin-derived and N-containing pyrolysis products (Fig. 2) suggest that soil texture had an important influence on the development of SOM chemical characteristics during the incubation period. The decline in lignin derivatives as soil texture becomes finer is consistent with research and conceptual models suggesting that in coarse-textured soils the biochemical protection of SOM (recalcitrance due to the chemistry of SOM) is the primary mechanism controlling SOM dynamics (Six et al., 2002). This suggests that lignin will represent a high proportion of SOM in sandy soils because it is biochemically protected and more difficult to decompose than other constituents of SOM. In contrast, in soils with a high clay content, stabilization by physical and chemical mechanisms, including aggregation, sorption on mineral surfaces, and entrapment within fine pores, will be the primary control over C accumulation (Mikutta et al., 2006; von Lützow et al., 2006). As such, compounds that interact directly with mineral surfaces (e.g. polysaccharides and N-containing compounds) should be more common in those soils with a higher potential for organo-mineral interactions (Kleber et al., 2007). These interactions confer greater stability than chemical recalcitrance (von Lützow et al., 2006; Marschner et al., 2008); as a result, lignin will be, as we observed, present in lower proportions in fine-textured soils.

N-containing compounds, particularly those derived from microorganisms, are among those capable of stabilization on mineral soil surfaces (Quiquampoix, 2000; Mikutta et al., 2006; Simpson et al., 2007) and many studies have shown that silt and clay fractions have narrower soil C:N ratios than sand fractions (Guggenberger et al., 1995). If interaction with clay surfaces is the primary mechanism underlying N persistence in soils, we would expect that as clay concentrations increase the relative abundance of N should also increase; a pattern consistent with our results. Other scientists have also found that soil texture and structural formation can influence SOM chemistry. For example, Kolbl and Kögel-Knabner (2004) demonstrated using CPMAS C-13 NMR that proportions of O-alkyl C increase and proportions of aryl C decrease with increasing soil clay contents. Likewise, Golchin et al. (1994) demonstrated differences in the chemistry of inter- and intraaggregate SOM. Grandy and Neff (2008) further explored such patterns by developing a conceptual model that demonstrates how soil aggregate formation and turnover could influence the chemistry of soil organic matter.

Differences in the chemistry of SOM components suggest that they should show a range of susceptibilities to decomposition. We correlated labile pool C with SOM chemistry to gain insights into which compounds were being utilized during the incubation period.

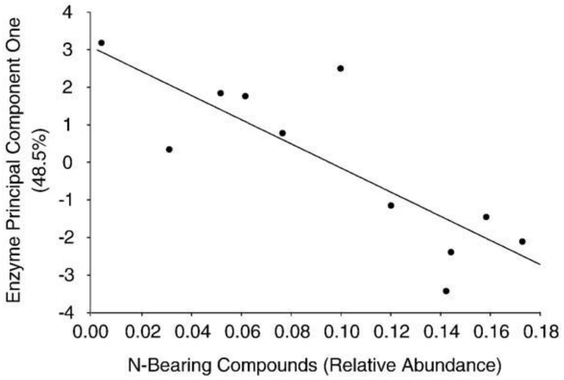

Fig. 3. Relationship between N-bearing compounds and the first principal component describing soil enzyme activities.

We found a positive correlation between N-bearing compounds prior to incubation and labile C but no other significant correlations with any chemical class. We also looked at correlations between labile C and the changes in relative abundances of the different chemical classes and found no relationships. Our results confirm that SOM N content is an important control over decomposition but also point to the difficulty associated with making generalizations about SOM decomposition based on chemistry alone. While litter decomposition rates can be accurately predicted by structural information, the chemical and physical protection of C and N in soils likely confounds similar empirical relationships for the decomposition of SOM.

4.2. SOM chemistry, enzymes, and fungal:bacterial ratios

The relative abundances of lignin and N-bearing compounds were not only correlated with soil texture, they were also correlated with soil enzyme activities. Prior to incubation, N-bearing compounds were strongly correlated with four of the six enzymes while lignin derivatives were negatively correlated with two of the enzymes. Grandy et al. (2007) also showed consistently strong relationships between the abundance of N-bearing compounds and enzyme activities including several examples where lignin derivatives were negatively correlated with enzyme activities. The strength of the relationship between overall enzyme activity and N-containing compounds is summarized by the relationship between the first principal component of all the enzyme activities and the relative abundance of N-containing compounds (Fig. 3). This principal component, which explained 48.5% of the variability (factor coordinates of the variables for principal component one: BG, −24; LAP, −2; NAG, −15; PHEN, −80; PER, −178), was very strongly related to the relative abundance of N-bearing compounds (Fig. 3).

Beta-glucosidase (BG) was among the enzymes showing a very strong relationship ($r=0.88$) with N-containing compounds. Grandy et al. (2007) also showed significant relationships between BG and N-containing compounds in a range of distinct soil types. This enzyme catalyzes the hydrolysis of terminal 1,4 linked ß-D-glucose residues from ß-D-glucosides. One possible explanation for this correlation is that microbial cells may be such a significant source of pyrroles that high microbial biomass or high biomass turnover could increase BG and pyrroles, resulting in a positive but indirect relationship between BG and N-containing compounds. Our results support this hypothesis: BG tended to be higher in the hardwood forests, which also had the highest microbial biomass. Another possibility is that BG also attacks short chitin oligomers.

Relationships between fungal:bacterial ratios and individual pyrolysis products suggest that changes in fungal:bacterial ratios may be directly linked to SOM chemistry and management. Fungal:bacterial ratios were lower in the pasture and cultivated sites than the forest sites and were positively correlated with lignin derivatives (4-acetylguaiacol, 4-propan-2-one-guaiacol, and guaiacol) and negatively correlated with the N-bearing compounds (pyridine and pyrrole). There are several plausible explanations for these relationships but the most parsimonious may be that the environment for decomposition favors fungi where soil disturbance is low and both lignin inputs and soil C/N ratios are high, as they are in the forest ecosystems. Fungi are very sensitive to soil disturbances that disrupt their hyphae (Bossuyt et al., 2001; Bailey et al., 2002; Emmerling, 2007) and the majority of lignin decomposition is known to occur via fungal rather than bacterial pathways (Kirk and Farrell, 1987; Lopez et al., 2006). A second and related explanation is that where N-bearing compounds are relatively more abundant it is common to see an increase in decomposition rates (Melillo et al., 1982; Trinsoutrot et al., 2000), as well as an increase in the abundance of bacteria, which tend to gain a competitive advantage in environments with rapid organic matter decomposition (Sinsabaugh et al., 2002). Both of these explanations highlight the potential for litter quality to drive microbial communities. A third explanation, which is not exclusive of the others, is that SOM C:N ratios may be lower in environments where bacteria are dominant because they have lower biomass C:N ratios than fungi (Cleveland and Liptzin, 2007). At any point in time, microbial biomass is a small proportion of total SOM (Cleveland and Liptzin, 2007) but microbially-derived inputs may be a substantial proportion of total SOM because of their preservation in soils (e.g. Simpson et al., 2007). Our results support those from other studies (Bossuyt et al., 2001; Bailey et al., 2002) suggesting that agricultural practices and the composition of SOM may influence fungal:bacterial ratios (and vice versa), but these are among the first results to show using spectroscopic methods that the abundance of specific N-bearing compounds and lignin derivatives are associated with fungal:bacterial ratios.

Other studies have shown that organic N content, determined by combustion, is related to soil microbial biomass, litter decomposition rates, and nutrient cycling (Melillo et al., 1982; Trinsoutrot et al., 2000) and previous work at these sites in South Carolina showed that fungal community structure was correlated with C:N ratios (Lauber et al., 2008). Together these results suggest that structural N plays a critical role in the development of, or is itself shaped by, microbial community composition, microbial enzyme activities, and the rate of biogeochemical processes. These results are supported by studies in cropping systems where the inclusion of legume cover crops with high N contents frequently changes microbial processes and C and N cycling relative to cropping systems that do not include leguminous cover crops (Drinkwater et al., 1998; Grandy and Robertson, 2007).

5. Summary and conclusions

Many studies have compared soil biological and biogeochemical processes associated with different kinds of land use on the same soil type (e.g. West and Post, 2002; Miller et al., 2004; Grandy and Robertson, 2007). These studies provide insight into the potential for changes in land use to influence soils that have similar edaphic properties. However, under most conditions, land use intensity in agricultural landscapes reflects the potential productivity of a site and soils under different land-uses are likely to have distinct edaphic properties. Highly productive soils tend to be used for agriculture while coarse textured soils with low nutrient availability and reduced water holding capacity are more likely to be converted to pasture or pine forests. Further, many soils that are broadly classified under the same type of land use (e.g. row-crop agriculture, pine forest, or pasture) are, in fact, managed differently with respect to crop rotation, tillage, and external inputs. Our study reflects the different kinds of management that are common to soils of varying productivity in the Piedmont Region of South Carolina. We demonstrate that variation in biogeochemical processes in the top 7.5 cm of mineral soil due to general changes in land use type is not sufficient to obscure variation due to differences in edaphic soil properties and specific management practices. Many soil properties that tend to differ between cultivated agricultural sites and pasture or pine forests (e.g. total C, MBC, and enzyme activities) were similar across these three land uses in the South Carolina Piedmont, likely because of variation in soil texture and other edaphic soil properties. Our results demonstrate that more effort should be made to study SOM dynamics, especially as they relate to C sequestration and offsetting increases in atmospheric CO_2, under realistic land use scenarios. While it is reasonable to expect substantial soil C gains at many sites where agricultural lands are converted to forests or pasture, the extent of this increase may be relatively minor in coarse-textured soils and may be highly dependent on the specific management practices implemented. Our study demonstrates that SOM dynamics cannot be predicted by land use intensity alone and that, where soil edaphic properties vary across a landscape, soil texture and the characteristics of the microbial communities can have an overarching influence on SOM chemistry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.geoderma.2009.02.007.

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