CHANGES IN BARK COMPOSITION FROM LONG-TERM ELEVATED CO_2 TREATMENT: IMPLICATIONS FOR THE MANAGEMENT OF SWEETGUM AS A WOOD ENERGY CROP

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Tree bark is comprised of living inner bark (phloem) that transports the products of photosynthesis and dead outer bark that protects the living tissues and seals in moisture. Active and passive defenses against destructive agents (e.g., insects, fungal pathogens) are provided by the inner bark and outer bark, respectively (Eberhardt 2013). For sweetgum (*Liquidambar styraciflua* L.), the bark comprises 23 percent by mass of the sapling-sized stems and 31 percent of the branches (Koch 1985); the percentage of bark in larger trees would be less. Trees debarked during processing by the forest products industry sector generate significant amounts of bark residue for conversion to mulch products or for fuel value recovery. The chemical composition of tree bark is important as it has the potential to significantly impact the utilization of bark, particularly for biofuel applications.

Sweetgum is a medium to large tree that grows best on moist sites, but can tolerate low moisture and nutrient availabilities. Adaptability to a wide range of site conditions makes it the preferred hardwood for bioenergy production despite its slower growth rate than other hardwoods such as cottonwood and sycamore (Kline and Coleman 2010). The effects of long-term elevated-CO_2 treatment on the inner and outer bark chemistry of sweetgum trees were investigated by the authors in a recent study (Eberhardt and others 2015). In a continuation of this work, ash, carbon, and hydrogen analyses are presented in the context of biofuels, and nitrogen content is presented since the demand for this macronutrient is relevant to the management of sweetgum as a wood energy crop. Furthermore, the application of principal component analysis (PCA) has been included as a technique to detect differences in spectroscopic data collected from the bark tissues both before and after extraction.

Inner and outer bark was collected from sweetgum trees harvested at the Oak Ridge National Laboratory sweetgum Free-Air CO_2 Enrichment (FACE) study site in Roane County, TN. Elevated-CO_2 treatment (*ca.* 550 ppm) was applied during the daytime, April through October, for more than a decade. Ash content was determined by combustion (525 °C, 6h). Carbon, hydrogen, and nitrogen concentrations were determined using a CHNS/O analyzer. One-way ANOVA of plot means used PROC GLM in SAS/STAT®9.3 ($P_\alpha < 0.1$ being significant). Multivariate analysis was performed on Fourier transform infrared (FTIR) spectroscopic data using Unscrambler 8.0 software.

Similar to that observed in sweetgum wood from a corresponding FACE study (Kim and others 2015), a higher ash content was observed for sweetgum inner bark with the elevated-CO_2 treatment (table 1); no difference was observed for the outer bark. Increases in ash content are disconcerting due to the negative impact on the utilization of woody biomass. The presence of ash can lead to excessive tool wear during lumber production (Porankiewicz and others 2006), and the formation of deposits during pulp and paper processing operations (Biermann 1996). As for biofuel applications, ash sintering during combustion causes problems in boilers (Lestander and others 2012), poisons catalysts used for biofuel conversions/syntheses (López-González and others 2014), and leads to the accumulation of heavy metals in biofuel byproducts thereby causing disposal issues (Liu and others 2015). To date, little is known about the effects of elevated CO_2 on biomass energy content in forest plantations (Calfapietra and others 2009). We found that the elevated-CO_2 treatment was associated with lower contents of carbon and hydrogen in the inner bark (table 1). Compared to fossil fuels, the higher heating value for biomass is lower due to relatively high hydrogen/carbon and oxygen/carbon ratios

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Table 1—Ash, carbon, hydrogen, and nitrogen analyses of sweetgum inner and outer bark samples from a FACE study site in Tennessee

		Ash	Carbon	Hydrogen	Nitrogen
		--------------------	--------------------%	--------------------	--------------------
Inner bark	Ambient CO_2	8.1 ± 0.1	40.1 ± 0.3	5.1 ± 0.2	0.32 ± 0.01
	Elevated CO_2	10.8 ± 1.0	35.9 ± 1.5	4.4 ± 0.3	0.24 ± 0.04
	P_α value	0.062	0.064	0.092	0.149
Outer bark	Ambient CO_2	7.1 ± 0.2	46.2 ± 0.2	5.2 ± 0.2	0.42 ± 0.00
	Elevated CO_2	7.9 ± 0.8	46.1 ± 0.5	5.2 ± 0.1	0.35 ± 0.01
	P_α value	0.336	0.856	0.542	0.016

(Basu 2010). Overall, these results suggest that the elevated-CO_2 treatment lowered the quality of bark for thermochemical conversions (combustion, pyrolysis, gasification, liquefaction) by an increased mineral content coinciding with decreased carbon levels.

While nitrogen concentrations were not different for the inner bark from the two CO_2 treatments, they were lower for the outer bark receiving the elevated-CO_2 treatment (table 1). Sweetgum with elevated CO_2 has shown increased productivity (Norby and others 2002) and increased root biomass/distribution (Iversen 2010) for nutrient extraction from the soil (Garten and others 2011). Decreased foliar nitrogen content (Norby and Iverson 2006), and also decreased nitrogen content of the outer bark are indicative of the constraints placed on nitrogen availability. Increased management intensity (e.g., weed control, weed control with irrigation, etc.) affords increased productivity in sweetgum stands and increased soil carbon and nitrogen by accelerated litter and root formation (Johnsen and others 2013). With intensively-managed hardwoods there can be timing issues whereby the time that the nitrogen is available in the soil is not the same as when it is needed by the tree (Scott and others 2004). Balancing nitrogen supply and demand for short-rotation sweetgum plantations will likely warrant greater attention to offset any exacerbation higher nitrogen demand from higher atmospheric CO_2 concentrations (Grant 2013).

Biochemical routes (e.g., fermentation) to generate biofuels from biomass are dependent upon the relative proportion of basic chemical constituents, those being cellulose, lignin, hemicelluloses, along with non-structural biomolecules that can be isolated by extraction with organic solvents, the so-called extractives. A discussion of these constituents is beyond the scope of this report; however, PCA of FTIR spectroscopic data from the inner and outer bark before and after extraction are provided to demonstrate the potential magnitude of chemical changes from the elevated-CO_2 treatment. The PCA scores plot (fig. 1) shows that the technique was able to differentiate between both sample processing (unextracted vs. extracted) and bark type (inner vs. outer bark); however it was unable to differentiate between elevated- and ambient-CO_2 treatments. Accordingly, while there may be chemical changes in the inner or outer bark tissues in response to the elevated-CO_2 treatment, it is unlikely that those changes would be significant enough to impact biochemical routes to generate biofuels.

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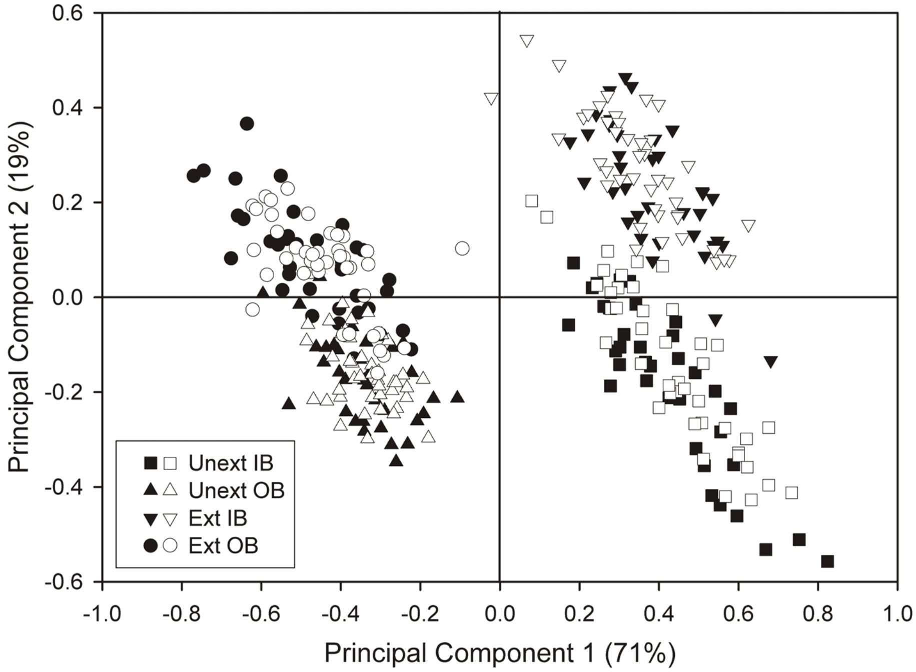

Figure 1—PCA scores plot of FTIR spectra from both unextracted (Unext) and extracted (Ext) inner (IB) and outer bark (OB) undergoing elevated- (filled shapes) and ambient-CO_2 (open shapes) treatments.

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