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Research paper

Carbohydrate and nutrient composition of corn stover from three southeastern USA locations

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ABSTRACT

Corn (*Zea mays* L.) stover has been identified as an important feedstock for bioenergy and bio-product production. Our objective was to quantify nutrient removal, carbohydrate composition, theoretical ethanol yield (TEY) for various stover fractions. In 2009, 2010, and 2011, whole-plant samples were collected from one field study in South Carolina (SC) and two in Alabama (AL). Soils at the SC site were classified as a Coxville/Rains-Goldboro-Lynchburg association, while those in AL were either Compass or Decatur. Plants were collected from two 1-m row segments, ears were removed and shelled. A portion of the remaining stalks were dried and ground to represent whole-plant stover. The remaining stalks were fractionated into stalk and leaf biomass from below the ear (bottom), stalk and leaf biomass from above the ear (top), cobs, and grain. A fifth sample representing "above-ear" biomass that might be collected mechanically was calculated using the weight ratios of the top and cob fractions. Carbohydrate and nutrient concentrations were estimated using near-infrared spectroscopy (NIRS) and TEY was calculated. The distribution of carbohydrates, nutrients, and TEY varied significantly among the corn stover fraction and research locations. This indicates that site-specific sampling and analysis should be used to optimize bioenergy and bio-product utilization of corn stover. However, at every location, the above-ear stover fractions were most desirable for cellulosic ethanol production. Furthermore, harvesting only above-ear stover fractions would reduce nutrient removal by 24–61% when compared to harvesting all stover biomass.

1. Introduction

Corn production in the southeastern U.S.A. does not rival that of the Corn Belt, but due to a much longer growing season and local markets associated with poultry and swine production, it is a relatively abundant crop. The long growing season throughout this region also makes it very feasible for double-cropping or incorporating a rye (*Secale cereale* L.) cover crop [1,2].

As corn grain production increases, the amount of stover available for bioenergy and/or bio-product development also increases. To facilitate industries investing in these potential uses [3], more information regarding stover composition and variation among geographic locations is needed. Furthermore, if corn stover is going to be harvested it is important to quantify the additional carbon and nutrient removal to prevent soil degradation through soil organic matter loss or the development of unexpected nutrient deficiencies. Quantifying potential nutrient removal through stover harvest is also important for designing manure management practices that do not result in excess nutrient accumulation and potentially greater losses to surface and subsurface water resources through surface runoff and/or leaching.

Corn stover, as any form of plant biomass, is composed of cellulose, hemicellulose, lignin, ash, and extractives [4]. Cellulose and hemicellulose are the most desirable portions of biomass for

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bioethanol conversion [5,6]. Cellulose is homogenous and composed of glucose monomers linked by glycosidic bonds. Hemicellulose is composed of 5-C (xylose and arabinose) and 6-C monomers (glucose, galactose, and mannose). The 6-C carbohydrates are more desirable for bioethanol production due to their higher conversion efficiency. The proportions of the carbohydrates in the plant seem to vary among different fractions [7] Corn biomass yield and composition can also vary with variety, and management practices [8]. Drought stress [9], planting densities [10], and crop development stage [11] can also affect biomass yield and composition. In the southeastern USA, corn yields often fluctuate widely in response to temporal weather variability [12] and spatial soil variability [13].

Quantifying carbon and nutrient removal is becoming more important to ensure long-term sustainability of soil resources as harvesting corn stover for biofuel or bio-products becomes a standard management practice. Corn residue left in the field supports several ecosystem services including: supporting microbial processes, minimizing wind and water erosion, sequestering carbon and cycling nutrients; functions that influence soil productivity [14–18]. To mitigate potential negative impacts of harvesting stover on soil properties, research studies have been conducted to determine where and what amount of crop residue can be sustainably harvested [19,20].

Our objective was to quantify nutrient and carbohydrate composition, and theoretical ethanol yield (TEY) for various stover fractions collected in three continuous corn studies at locations in the southeastern U.S.A.

2. Materials and methods

2.1. Site description

This study was conducted from 2009 to 2011 at two locations in Alabama (AL) and one in South Carolina (SC). The first AL location was the E.V. Smith Research Center (EVS) in central Alabama (32.43 N, −85.89 W) which has a mean annual precipitation (MAP) of 1330 mm and mean annual temperature (MAT) of 18 °C. The second was the Tennessee Valley Research and Extension Center (TVS) in Belle Mina (34.69 N, −86.89 W) in the northern part of the state which has a MAP of 1380 mm and MAT of 16 °C. The soil at EVS was a Compass loamy sand (Coarse-loamy, siliceous, subactive, thermic Plinthic Paleudults), while at TVS, it was a Decatur silt loam (Fine, kaolinitic, thermic Rhodic Paleudults). The SC study was at the Clemson University Pee Dee Research and Education Center (PDREC) in Florence (34.28 N, −79.74 W) which has a MAP of 1300 mm and MAT of 17 °C. The PDREC site had several soil map units within the experimental site, but collectively the comprised a typical Coxville/Rains-Goldsboro-Lynchburg soil association. Table 1 shows the seasonal cumulative precipitation and seasonal average temperature during the three growing seasons at each location.

Table 1
Seasonal cumulative precipitation and average temperature at the Pee Dee Research and Education Center in South Carolina (SC), E.V. Smith Research and Extension Center (EVS) in central Alabama, and the Tennessee Valley Research and Extension Center (TVS) in northern Alabama.

Location	Year	Cumulative precipitation (mm)	Average temperature (°C)
SC	2009	648	24.0
	2010	693	25.9
	2011	293	26.0
EVS	2009	976	24.3
	2010	514	25.8
	2011	427	26.4
TVS	2009	808	22.6
	2010	367	24.8
	2011	329	25.5

Five corn residue removal treatments (0, 25, 50, 75, and 100%) were replicated four times on 137.6 m^2 plots using a randomized complete block design at the PDREC. For this study, however, only the 0 and 100% removal treatments were sampled. Both sites in AL were arranged in a split-plot design with 3 replications with plots 16.7 m^2 in size. Main plots consisted of cereal rye as a winter cover with three levels (no cover, rye as a cover crop harvested in spring, and rye retained after chemical termination with glyphosate), and sub-plots were two corn residue removal levels (0 and 100% removal). For this study the two main treatments were averaged. A single N fertilizer rate of 168 kg ha^{-1} was applied to all plots in both states. In late winter of every year in AL, 34 kg ha^{-1} N was applied to all plots with cereal rye as a winter cover. DeKalb C69-71 corn hybrid was grown at the PDREC, while Pioneer 31G65R was grown at both AL locations. Urea ammonium nitrate (UAN 28-0-0) was used as the nitrogen source in all three sites. Phosphorus and K were applied based on soil test results. The PDREC crops were grown without irrigation, but included annual in-row subsoiling to a depth of 30–40 cm. In AL, corn was grown using no-tillage practices without irrigation each year.

2.2. Sample collection

Corn plants at PDREC were harvested at physiological maturity while those at EVC and TVS were harvested just before grain harvest between mid-September to mid-October depending on the year and location. Plants were collected from two 1-m row segments, ears were removed, and shelled. A portion of the remaining stalks were dried and ground to represent whole-plant stover. The remaining stalks were fractionated into stalk and leaf biomass from below the ear (bottom), stalk and leaf biomass from above the ear (top), cobs, and grain (Fig. 1). A fifth sample representing "above-ear" biomass that might be collected mechanically was calculated using mass-weighted ratios of the top and cob fractions. All plant samples were oven dried for approximately seven days at 55–60 °C or until constant weight was achieved. Samples were then ground using a Wiley mill to pass through a 2 mm sieve.

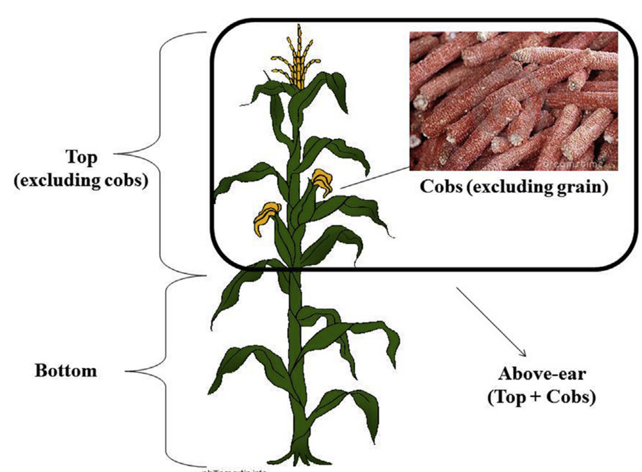

Fig. 1. Partitions of the corn plant that used in this study. The image of the plant has been adapted from: http://biology.phillipmartin.info/biology_corn_plant.html (accessed 10/14/2015). The image of the cobs has been adapted from: http://www.dreamstime.com/royalty-free-stock-photo-corn-cob-image969295 (accessed 10/14/2015).

2.3. NIR preprocessing

Near-infrared spectroscopy (NIRS) techniques were used for sample analysis. To ensure appropriate NIR calibration that would capture a wide range of compositional characteristics, ground samples from all three locations (~400), along with 2100 corn tissue samples from other experiments were scanned and analyzed with a FOSS 5000 NIRS instrumentation using the ISIscan™ and WinISI 4 software (© FOSS Analytical AB 2004). After scanning all the samples, the Standard Normal Variate (SNV) and Detrend scatter correction in WinISI4 were used to reduce particle size effects and remove the linear and quadratic curvatures from the spectra. The spectra were then ranked according to the global Mahalanobis distance (GH) before selecting representative samples from the entire GH range which were chosen for wet chemistry analysis.

2.4. Chemical analysis

The C and N content of every sample was determined via dry combustion in a LECO TruSpec C/N analyzer (Leco Corp., St. Joseph, MI). The procedure described by Mourtzinis et al., was used to quantify the polymeric carbohydrates (glucan, xylan, mannan, galactan, and arabinan) [21]. This is a neutral detergent fiber (NDF) extraction [22] followed by a two-step acid hydrolysis of the extractive-free sample [23]. Samples were analyzed for monomeric carbohydrates using high pressure liquid chromatography (HPLC) with a Shimadzu HPLC (LC-20A) system outfitted with a degasser, autosampler, parallel double plunger pump (LC-20AD), and a refractive index detector (RID-10A) was used (Shimadzu Scientific Instruments Inc.-USA Headquarters, Columbia, MD). The detector was equipped with a HPLC carbohydrate analysis column specific for separation of monosaccharides derived from cellulose (Aminex HPX-87P, 8% cross-linked resin lead ionic form, 9 um particle size, pH range of 5–9, and 300 × 7.8 mm in size; Bio-Rad Life Science, Hercules, CA). A compatible guard column was utilized from the same manufacturer. The mobile phase consisted of water at a 0.6 ml/min flow rate. During elution the temperature of the column was maintained at 85 °C. Only glucose, xylose and arabinose were above the detectable limits, so this report focuses on these three sugars.

Another sub-sample was subjected to a microwave digestion procedure to determine aluminum (Al), manganese (Mn), calcium (Ca), zinc (Zn), sulfur (S), phosphorus (P), potassium (K), cupper (Cu), and magnesium (Mg) concentrations for the 400 samples using concentrated HNO_3 acid in a Mars Xpress Microwave Digester (CEM Corp., Mathews, NC, USA). The digestion procedure was based on the USEPA 3051A method [24]. All extracts were analyzed using an inductively coupled plasma-atomic emission spectrograph (ICP-AES). The energy content of the samples (MJ kg^{-1}) was quantified in the form of high heating value (HHV) via dry combustion in a Calorimeter System (IKA® C 2000 basic C 2000 control; IKA® Works, Inc NC, USA).

2.5. NIR calibration

The modified partial least squared (modified PLS) was found to be the most appropriate for interpreting NIR data for all the chemical components. The math treatment used for the calibration is known as the (1, 4, 4, 1) technique. This involves the 1st derivative, a 4 nm gap and 4 initial smoothing points, with no further smoothing. The standard error of calibration (SEC), the standard error of cross validation (SECV), and the coefficient of determination were used to evaluate the fit of the model and the accuracy of the obtained data (Table 2). The NIR technique successfully predicted concentrations for only K, P, S, Mg, and Ca, so this report focuses only on those minerals.

Table 2
Near-infrared calibration statistics for glucan, xylan, arabinan, potassium (K), phosphorus (P), sulfur (S), magnesium (Mg), and calcium (Ca).

Compositional attributes	[a]SEC	R^2	[b]SECV
Glucan	2.07	0.713	2.28
Xylan	1.31	0.896	1.48
Arabinan	0.44	0.827	0.51
K	642.77	0.962	798.65
P	181.16	0.817	203.59
S	59.14	0.911	69.70
Mg	149.90	0.963	169.71
Ca	220.76	0.952	269.81

[a] Standard error of calibration.
[b] Standard error of cross validation.

To further evaluate the accuracy of the developed models, an additional dataset (n = 160) of plant tissue with known carbohydrate content values was included and scanned in the NIRS with the stover samples. Known compositional values in these samples were compared to the NIRS-derived values. There was no significant difference between the actual and NIRS predicted values, which was an additional indication of the acceptable performance of the NIRS models.

The TEY was calculated using the carbohydrate concentrations in corn stover samples and the U.S. Department of Energy theoretical ethanol yield calculator (DOE). The calculator reports the TEY yield in gal Mg^{-1} of biomass, so values were multiplied by 3.785 to convert them to L Mg^{-1} of corn biomass. The formula can be found in Mourtzinis et al., 2014 [21].

2.6. Statistical analysis

This multi-location study was not designed nor intended to examine corn stover composition differences among locations, soil types, or between hybrids. Apart from the whole biomass (whole plant), four plant portions were of interest: the bottom portion (bottom); top portion excluding cobs (top); cobs alone (cob); and the plant portion above the first ear (above-ear), which was calculated as a weighted average of the top portion of the plant and the cobs. The weight of the above-ear fraction was a calculated value from the tops and cobs and the resulting partitions were not mutually exclusive, which mean that the weight of above-ears includes the weight of tops and cobs. Therefore, the compositional characteristics of the above-ear fraction were compared only against the bottom portion of the stover within locations. Repeated measures analysis of variance, utilizing the GLIMMIX procedure in SAS 9.3 (SAS for Windows v. 9.3, SAS Institute Inc., Cary, NC) and the AR (1) covariance structure, was used to detect differences between the bottom and above-ear biomass partitions carbohydrate composition, nutrient content, and TEY. A factor was considered to be significant at a level less than 0.05 (alpha = 0.05).

3. Results and discussion

3.1. Distribution of carbohydrates, and theoretical ethanol yield in corn biomass

The carbohydrate content in corn biomass was highly variable among the different plant portions at all three locations (Table 3). At all three locations the relative distributions of glucan, xylan, and arabinan among the different corn portions were similar. The highest glucan content was observed in the bottom portion of the plants while the above-ear portions had the highest xylan and arabinan content. The cobs, tops, and above-ear portions had the

Table 3
Three-year [mean (standard error)] carbohydrate content, biomass yield, and theoretical ethanol yield (TEY) for various fractions at the Pee Dee Research and Education Center in South Carolina (SC), the E.V. Smith Research and Extension Center (EVS) in central Alabama and the Tennessee Valley Research and Extension Center (TVS) in northern Alabama.

Location	SC					
	Glucan	Xylan	Arabinan	Biomass yield	TEY	TEY
	%			kg ha^{-1}	L Mg^{-1}	L ha^{-1}
Whole plant	45.4 (0.50)	22.7 (0.25)	1.9 (0.15)	9076 (385.8)	459.7 (1.6)	4180 (189.0)
Bottom	47.7 (0.32)	20.9 (0.18)	1.4 (0.12)	4248 (185.9)	460.7 (1.3)	1957 (87.9)
Top	41.0 (0.41)	25.3 (0.27)	2.8 (0.09)	3333 (149.5)	455.4 (1.9)	1509 (74.7)
Cob	37.9 (0.15)	29.0 (0.55)	2.7 (0.14)	1494 (77.9)	459.4 (3.2)	643 (48.9)
Above-ear	39.4 (0.26)	26.7 (0.29)	3.0 (0.08)	4828 (216.0)	456.0 (3.0)	2109 (148.4)
[a]Pr > F	<0.001	<0.001	0.001	0.137	0.184	0.497
Location	EVS					
Whole plant	42.5 (0.15)	22.0 (0.14)	2.2 (0.03)	4589 (163.4)	439.5 (1.5)	1995 (70.6)
Bottom	45.3 (0.23)	19.9 (0.11)	1.2 (0.07)	1556 (78.4)	436.1 (1.7)	670 (32.8)
Top	42.9 (0.13)	21.7 (0.11)	2.5 (0.03)	1996 (82.6)	442.0 (0.8)	887 (38.0)
Cob	37.1 (0.07)	27.0 (0.06)	2.8 (0.02)	1037 (31.1)	441.3 (0.4)	456 (14.6)
Above-ear	41.2 (0.15)	23.1 (0.13)	2.7 (0.04)	3033 (107.9)	441.7 (1.4)	1323 (47.5)
[a]Pr > F	<0.001	<0.001	<0.001	<0.001	0.180	<0.001
Location	TVS					
Whole plant	41.6 (0.23)	22.4 (0.18)	2.3 (0.05)	5227 (210.9)	437.3 (1.2)	2274 (89.0)
Bottom	44.6 (0.21)	19.7 (0.19)	1.1 (0.04)	1690 (125.7)	431.6 (0.8)	729 (56.3)
Top	42.9 (0.13)	21.7 (0.11)	2.5 (0.03)	2474 (80.3)	442.2 (0.8)	1088 (37.6)
Cob	37.1 (0.07)	27.0 (0.06)	2.8 0.02)	1076 (49.6)	441.3 (0.4)	471 (24.6)
Above-ear	40.3 (0.19)	23.7 (0.13)	2.8 (0.04)	3550 (109.1)	440.3 (1.1)	1555 (45.8)
[a]Pr > F	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

[a] The Pr > F values represent the probability of a larger F by chance between the bottom and above-ear fractions. The above-ear fraction, which was calculated as a weighted average of the top portion of the plant and the cobs, was not mutually exclusive from the tops and cobs, and its compositional characteristics were compared only against the bottom portion of the stover within locations.

highest TEY (L Mg^{-1}) in biomass grown at both locations in Alabama; while in SC there were no significant variations. Due to the high variability in biomass yields in every location (Table 3), a comparison of TEY per unit area (L ha^{-1}) is more appropriate. Between the two major plant portions, the bottom and above-ear, the later resulted in the highest TEY, this was 2109, 1323, and 1555 L ha^{-1} in SC, EVS, and TVS respectively (Table 3). The bottom plant portion resulted in the second highest cellulosic ethanol yield potential in SC, while in both sites in Alabama it was the top portion that exhibited the second highest TEY (L ha^{-1}).

It seems that the effect of biomass yield on TEY per unit of area (L ha^{-1}) is far more important than the effect of carbohydrate concentration. A similar conclusion was reported in an experiment which was investigating the ethanol potential of herbaceous biomass in North Dakota [8]. Furthermore, the results reported are in agreement with the results of a similar study which was conducted in Iowa [7]. In that study the highest glucan content (37.6%) was also observed in the bottom plant portion and the lowest glucan concentration (33.7%) was detected in the above-ear biomass. In the same study, the TEY per unit of area ranged from 757 to 3002 L ha^{-1} with the above-ear portion yielding the highest cellulosic ethanol yield potential (2135 L ha^{-1}).

Despite the similarities between the two studies in the relative distribution of carbohydrates and TEYs among the different plant fractions, the carbohydrate concentrations which were reported by Reed et al. [7] are lower than those reported in this study. Therefore, it should be noted that they harvested the corn samples from a site near Ames, IA where the climate is considerably different than that of the southeastern US. Furthermore, it is known that the compositional characteristics of the plant vary with the growth stage of the plant [11]. In their study, the researchers collected the corn samples at R6 growth stage from a site where the previous year crop was soybean [*Glycine max* (L.) Merr.]. Also, they used a Fontenell 5393 corn hybrid which could result in different compositional characteristics from the DeKalb and Pioneer used in SC and Alabama sites respectively.

3.2. Distribution of carbon and nutrients in corn biomass

When the goal of an agricultural system is sustainable corn stover harvest for biofuel and grain production, it is desirable to harvest a high amount of biomass without impacting soil quality. Intuitively then, a portion of the stover with high TEY (L ha^{-1}) and low amounts of C, N and nutrients would qualify as a desirable biofuel feedstock. In all three locations of this study, there were differences in the relative distributions of C, N and nutrients in corn biomass (Table 4). In every location, the highest C content was observed in the cobs while the tops exhibited the highest N concentrations. The bottom plant portions seemed to have the highest K and P contents. The highest S content was detected in the upper plant portions while Mg and Ca appeared to be evenly distributed between the bottom and above-ear fractions of the corn plants. These results are in agreement with a similar multi-location nutrient removal study [25].

As mentioned in the previous section, the biomass yield seems to be the most important factor in the maximization of cellulosic ethanol production. Therefore, estimation of the amount of C, N, and nutrients that would be removed in different biomass harvesting scenarios is essential. Such an assessment would allow for an estimation of the component quantities that would have to be replaced in the soil to maintain long-term productivity. The scenario of harvesting the cobs alone, which have been recognized as a desirable feedstock for biofuel conversion [26], would result in the lowest removal rates of C, N and other elements in all three locations of the study (Table 4). However, this would be a result of their low yield. The top portion of the stover would result in a high partial biomass harvest; however, it does not appear sensible to exclude the cobs due to their low lignin and ash content and their high holocellulose content [27]. Therefore, of all the portions of the stover, the bottom and above-ear partitions, that have the highest biomass yields, could be attractive feedstocks for sustainable cellulosic ethanol production.

At all three locations, harvesting the above-ear biomass, which

Table 4
Three-year [mean (standard error)] carbon and nutrient removal estimates for various corn stover fractions at the Pee Dee Research and Education Center in South Carolina (SC), the E.V. Smith Research and Extension Center (EVS) in central Alabama and the Tennessee Valley Research and Extension Center (TVS) in northern Alabama.

Location	SC						
Element	C	N	K	S	P	Mg	Ca
	$kg\ ha^{-1}$						
Whole plant	4843.5 (133.3)	59.8 (5.2)	117.0 (5.7)	5.8 (0.1)	7.2 (0.8)	16.5 (0.9)	16.8 (0.7)
Bottom	2268.9 (66.1)	27.8 (1.7)	67.9 (5.3)	2.3 (0.1)	3.6 (0.4)	7.3 (0.3)	7.6 (0.3)
Top	1766.1 (59.6)	26.4 (2.4)	24.1 (1.8)	2.0 (0.1)	2.1 (0.2)	4.5 (0.3)	4.5 (0.2)
Cob	831.9 (31.5)	10.4 (1.0)	11.7 (0.8)	0.7 (0.04)	1.0 (0.1)	0.7 (0.06)	0.6 (0.08)
Above-ear	2614.5 (79.0)	35.7 (2.4)	41.0 (1.9)	3.6 (0.1)	3.6 (0.3)	8.7 (0.5)	8.8 (0.4)
[a]Pr > F	<0.001	<0.001	<0.001	<0.001	0.989	0.105	0.039
Location	EVS						
Whole plant	2117.8 (75.5)	46.8 (1.5)	33.6 (2.0)	4.3 (0.2)	3.3 (0.3)	5.2 (0.3)	7.6 (0.3)
Bottom	714.8 (35.1)	17.1 (0.9)	14.2 (1.2)	1.4 (0.1)	1.7 (0.1)	1.9 (0.1)	2.6 (0.1)
Top	914.4 (37.9)	23.0 (0.9)	12.1 (0.9)	2.4 (0.1)	1.2 (0.1)	2.2 (0.1)	3.7 (0.2)
Cob	483.5 (15.1)	8.4 (0.4)	8.2 (0.5)	0.7 (0.02)	0.6 (0.05)	1.2 (0.1)	1.5 (0.1)
Above-ear	1402.5 (51.0)	29.6 (0.8)	19.2 (1.1)	3.0 (0.1)	1.6 (0.2)	3.3 (0.2)	5.0 (0.2)
[a]Pr > F	<0.001	0.023	0.063	<0.001	0.692	<0.001	<0.001
Location	TVS						
Whole plant	2445.6 (98.2)	45.0 (2.5)	43.1 (3.3)	4.4 (0.2)	4.1 (0.3)	6.8 (0.5)	10.6 (0.6)
Bottom	795.4 (59.1)	14.7 (1.4)	17.8 (2.0)	1.1 (0.1)	1.6 (0.1)	2.4 (0.2)	3.5 (0.3)
Top	1141.4 (36.6)	22.4 (1.1)	17.9 (1.4)	2.6 (0.1)	1.8 (0.1)	2.9 (0.3)	5.6 (0.3)
Cob	512.5 (29.7)	8.9 (0.9)	7.2 (0.5)	0.7 (0.03)	0.6 (0.06)	1.2 (0.1)	1.5 (0.09)
Above-ear	1659.1 (52.8)	30.4 (1.4)	25.4 (1.7)	3.3 (0.1)	2.4 (0.2)	4.2 (0.3)	7.2 (0.4)
[a]Pr > F	<0.001	<0.001	0.178	<0.001	0.051	0.062	0.001

[a] The Pr > F values represent the probability of a larger F by chance between the bottom and above-ear fractions. The above-ear fraction, which was calculated as a weighted average of the top portion of the plant and the cobs, was not mutually exclusive from the tops and cobs, and its compositional characteristics were compared only against the bottom portion of the stover within locations.

has the highest partial biomass yield and the highest TEY (Table 3), would result in the largest removal of C, N, K, S, P, Mg and Ca. However, to put the numbers into perspective, removing the above-ear portion, when compared to the total stover harvest, would result in lower removal of elements by 24–61%, depending on the element and the location (Table 4). These removal rates, although slightly higher than those reported by Johnson et al., in 2010, follow the same pattern. Harvesting the bottom portion of the plant, which had the second highest yield after the above-ear, when compared to the total stover would result in lower removal of elements by 34–75%, depending on the element and the location (Table 4).

It is obvious that the most appropriate stover portion for sustainable biofuel production is a function of several factors. A feedstock that would result in the lowest possible removal of nutrients in combination with a high TEY would be highly attractive. Other important desirable attribute is low lignin content when the biochemical conversion route is to be followed. Therefore, it is interesting to compare the nutrient removal rates and cellulosic ethanol potential of the two major stover portions, bottom and above-ear. During the three years of the experiment, harvesting the above-ear partition would result in up to 51% higher TEY than the bottom portion, depending the location (Table 3). The significantly lower lignin content by 2.8–4% and lower ash content by 0.4–1.1% of the above-ear fraction when compared to the bottom stover is also a highly desirable characteristic [27]. However, choosing to harvest the above-ear biomass would result in significantly higher C, N, and S removal rates than harvesting the bottom part (Table 4). Nevertheless, the combination of high yield, high TEY, and low lignin content, significantly reduced C and nutrient removal rates of the above-ear portion when compared to the whole biomass, indicate its superiority as a possible sustainable biofuel feedstock. This conclusion is also in agreement with other previous studies [25,28,29].

It should be noted that estimating the nutrient removal rates using only plant composition data can lead to incorrect projections on soil quality impacts. Consistent stover removal has been reported to decrease soil N mineralization rates [30,31] and eventually to decrease the soil organic N content [32,33]. Therefore, monitoring and evaluating changes of soil nutrient status as a function of stover harvest should be an essential part of biofuel sustainability research.

4. Conclusions

The objective of this study was to evaluate the variability of nutrients and carbohydrates content, and biofuel potential in total and partial corn biomass in the southeastern US. There were significant differences in carbohydrate concentrations among different corn stover fractions. However, these variations had little to no effect on TEY ($L\ Mg^{-1}$ of biomass). Results in this study suggest that the amount of biomass is the most significant factor that influences the TEY in AL and in SC. The above-ear portion resulted in the highest TEY ($L\ ha^{-1}$) at every location of the study. Furthermore, harvesting the above-ear stover portion would lead to significantly lower C and nutrient removal rates than removing the total stover in AL and in SC. Nevertheless, the results reported in this manuscript concern the Pioneer and DeKalb corn hybrids which were grown at the specific locations. Generalizations and comparisons to other corn hybrids grown in different climates and soil types should be avoided.

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