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ORIGINAL RESEARCH

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Key environmental and production factors for understanding variation in switchgrass chemical attributes

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Abstract

Switchgrass (*Panicum virgatum* L.) is a promising feedstock for bioenergy and bioproducts; however, its inherent variability in chemical attributes creates challenges for uniform conversion efficiencies and product quality. It is necessary to understand the range of variation and factors (i.e., field management, environmental) influencing chemical attributes for process improvement and risk assessment. The objectives of this study were to (1) examine the impact of nitrogen fertilizer application rate, year, and location on switchgrass chemical attributes, (2) examine the relationships among chemical attributes, weather and soil data, and (3) develop models to predict chemical attributes using environmental factors. Switchgrass samples from a field study spanning four locations including upland cultivars, one location including a lowland cultivar, and between three and six harvest years were assessed for glucan, xylan, lignin, volatiles, carbon, nitrogen, and ash concentrations. Using variance estimation, location/cultivar, nitrogen application rate, and year explained 65%–96% of the variation for switchgrass chemical attributes. Location/cultivar × year interaction was a significant factor for all chemical attributes indicating environmental-based influences. Nitrogen rate was less influential. Production variables and environmental conditions occurring during the switchgrass field trials were used to successfully predict chemical attributes using linear regression models. Upland switchgrass results highlight the complexity in plant responses to growing conditions because all production and environmental variables had strong relationships with one or more chemical attributes. Lowland switchgrass was limited to observations of year-to-year environmental variability and nitrogen application rate. All explanatory variable categories were important for lowland switchgrass models but stand age and precipitation relationships were particularly strong. The relationships found in this study can be used to understand spatial and temporal variation in switchgrass chemical attributes. The ability to predict chemical attributes critical for conversion processes in a geospatial/temporal manner would provide state-of-the-art knowledge for risk assessment in the bioenergy and bioproducts industry.

KEYWORDS
bioenergy, drought, environmental explanatory variables, lowland ecotype, nitrogen, production factors, Regional Feedstock Partnership, upland ecotype

1 | INTRODUCTION

Biomass production is being pursued in the United States and worldwide to supply renewable energy resources, support reduced fossil fuel usage, meet national energy security policies, and provide potential environmental benefits (Demirbas, 2009; United States Congress, 2007). Second-generation perennial energy crops are of particular interest for use in bioenergy and bioproducts because of their potential environmental benefits. These include carbon sequestration and the capacity to grow on land that is marginal for food crops and vulnerable to environmental degradation (Bessou et al., 2011; Gelfand et al., 2013; Tilman et al., 2006). Switchgrass is a perennial grass species of interest for biomass production in North America because it is native and has potential for high biomass yields. The species also grows well on marginal lands, tolerates low-nutrient soils, and even displays promising responses to water stress (Barney et al., 2009; Wright & Turhollow, 2010).

Meeting biomass supply is often considered the critical factor for developing a bioenergy industry, and the best-case scenario for a bioenergy facility would be a consistent supply of biomass that can meet process specifications (Cundiff et al., 2009). Switchgrass has potential to produce high biomass yields; however, yields can vary by location and from year to year as a result of factors such as cultivar, climate, extreme weather events, soils, disease, production/management practices, and field history (Fike et al., 2017; Hong et al., 2014). Some control can be exerted by selecting ecotypes with properties better suited for the growing conditions. Lowland ecotypes have greater yield potential than upland ecotypes if planted where they are well adapted (Lee et al., 2018). Lowland ecotypes are adapted to lower elevations and latitudes and wetter climates, whereas upland ecotypes are better suited for sites with higher elevations, greater latitudes, and drier environments (Casler et al., 2004; Sanderson et al., 1996).

Although appropriate pairing of cultivars or ecotypes with local or regional growing conditions can help mitigate low or variable biomass yields, ecotypic differences may have feedstock quality implications. That is, different cultivars or ecotypes could affect the chemical attributes of the feedstock given that lowland switchgrass is larger and upland switchgrass is shorter with thinner stems that have the potential to be less lignified (Hong et al., 2014; Lee et al., 2018). Along with chemical and physical attribute differences due to ecotype, variability in these attributes also results from plant responses to field management practices and environmental conditions. Hong et al. (2014) found that location and year affected cellulose, hemicellulose, lignin, ash, and nitrogen concentrations; however, nitrogen fertilization rate had less of an impact. The effects of increasing nitrogen application rate on lignocellulosic concentrations have varied in field trials from no impact on hemicellulose, cellulose, and lignin within each month switchgrass was harvested (Ibrahim et al., 2017) to decreased hemicellulose (Hong et al., 2014; Lemus et al., 2008) to increased cellulose and lignin (Lemus et al., 2008; Waramit et al., 2011). A meta-analysis of more than 50 studies found that nitrogen addition decreased hemicellulose and increased lignin, but cellulose and non-structural carbohydrates remained unchanged (Liu et al., 2016). A recent study observed reduced hemicellulose, particularly xylose, in response to increased nitrogen application under ambient rainfall conditions; however, hemicellulose was unchanged with nitrogen application when precipitation was reduced by adding a

TABLE 1 Cultivar type, cultivar, planting date, and crop years with samples that have chemical material attribute data used in the study for each field location state

Cultivar type	Cultivar	Location	Planting date	Crop years
Upland	Cave-in-rock	Iowa	5/8/2009	2011–2013
	Cave-in-rock	New York	5/29/2008	2009–2014
	Blackwell	Oklahoma	9/2/2008	2010–2014
	Sunburst	South Dakota	5/17/2008	2009–2012, 2014
Lowland	Alamo	Virginia	7/1/2008	2009–2014

rainout shelter (Emery et al., 2020). Drought conditions have also decreased switchgrass lignin, glucan, and xylan concentrations and increased soluble sugar concentrations and extractive components (Ong et al., 2016). These later constituents may have antiquality effects because they can lead to the formation of pyrazines and imidazoles, known fermentation inhibitors, following ammonia fiber expansion (AFEX) pretreatment (Ong et al., 2016). In contrast, in another drought study no composition or reactivity effect was observed, perhaps due to drought severity or timing during the growing season (Hoover et al., 2018), or as a result of some level of drought tolerance in the species (Lewandowski et al., 2003; Wright & Turhollow, 2010). Growing degree days (GDDs) necessary for plant growth also impacts plant chemistry; Alamo and Cave-in-Rock switchgrass grown in Texas and Virginia had an increase in lignocellulosic components with degree days that occurred at the same time as internode elongation (Sanderson & Wolf, 1995). In contrast, protein, ash, and potassium decreased with more degree days. The varied results of these past studies demonstrate the complexity of how plants respond to the environment and production/management practices. Therefore, many environmental and production factors need to be considered simultaneously to understand the impact on biomass chemical attributes.

Biorefineries are open to substantial operational and economic risk when biomass has high variability in material attributes (United States Department of Energy, 2016). Given research findings that switchgrass yield and chemical attributes differ from year to year and across spatial extents, information regarding variability of biomass yield and chemical attributes over a longer period is needed for operational design and risk mitigation and management. This type of information is important for determining critical material attribute ranges necessary to build proper robustness into preprocessing and conversion unit operations at biorefineries and to determine economic impacts over time. To inform this problem, it is necessary to tease out the factors that have the largest impact on switchgrass chemical attributes, but few data sets exist with spatial and temporal data extensive enough to do this.

The overarching goal of this study was to understand the impact of sources of variability on switchgrass chemical attributes. To address this objective, chemical analysis was performed for switchgrass grown as part of the Sun Grant/DOE Regional Feedstock Partnership field trials that were planted in 2008 to address barriers to biomass supply for biorefineries. The field trials span five fields each in a different state over 6 years capturing diverse spatial and temporal environmental conditions. This study examines the variability in important bioenergy conversion chemical attributes and quantifies how these chemical attributes are impacted by nitrogen application rate, year, and location/cultivar. Further, this study used relationships among the biomass chemical attributes and weather—precipitation, drought, temperature—and soil variables to determine the primary factors impacting biomass chemistry and to derive models for predicting these biomass chemical attributes using publicly available data sets of these environmental factors. The study took into consideration as many known factors as possible; where information gaps existed, they were noted for consideration for future experiments. The various cultivars were grouped into upland and lowland ecotypes and investigated separately to account for genetic differences that are more broadly applicable to cultivars within these ecotypes not represented in these field studies.

2 | MATERIALS AND METHODS

2.1 | Biomass

Switchgrass was grown as part of the Sun Grant/DOE Regional Feedstock Partnership Field Trials that started in 2008 (Owens, 2018; Owens et al., 2016). Field locations for the study were selected where switchgrass was well adapted and productive, and the range of locations had diverse climatic and edaphic conditions (Owens, 2018). Lowland or uplands switchgrass cultivars were selected based suitability to each field location (Owens, 2018). Upland switchgrass cultivars were planted in Tompkins County, New York (42.462386, −76.460608); Muskogee County, Oklahoma (35.7425, −95.6392), and Day County, South Dakota (45.268965, −97.835825) in 2008 and in Story County, Iowa in 2009 (41.983056, −93.697232) (Table 1). A lowland switchgrass cultivar was planted in Pittsylvania

County, Virginia in 2008 (36.932296, −79.189968). The field study included three nitrogen fertilization levels—0, 56, and 112 kg N ha^{-1}—in a randomized complete block design with four replicate plots. Hong et al. (2014) and Fike et al. (2017) have additional details regarding field sites and management. Dry biomass yields for each plot were determined as described in Fike et al. (2017). Samples for chemical characterization were collected from windrows in Iowa from 2011 to 2013, New York from 2009 to 2014, and Virginia from 2009 to 2014. Samples were collected from bale cores in Oklahoma from 2010 to 2014 and South Dakota from 2009 to 2012 and in 2014. Stand age was calculated as the number of years since planting. Switchgrass samples for characterization were dried at 60°C for 48 h and then milled to pass a 2-mm sieve using a Thomas Model 4 Wiley Mill (Thomas Scientific, Swedesboro, NJ, USA).

2.2 | Chemical composition

Duplicates of each milled sample were placed in a desiccator at room temperature for a minimum of 72 h. A Thermo Antaris II FT-NIR with auto-sampler attachment and Omnic software (Thermo Scientific, Waltham, MA, USA) was used to collect 128 NIR spectra over wavenumbers 4000–10,000 cm^{-1} that were averaged to get one spectrum per duplicate sample. The resulting duplicate spectra were averaged to get a final spectrum per sample for prediction. Percent glucan (from cellulose and starch), xylan, and lignin were predicted using a mixed herbaceous feedstock partial least squares (PLS) 2 model built in Unscrambler X 10.3 software (Camo Software Inc., Woodbridge, NJ, USA). The PLS2 model has been described previously (Payne & Wolfrum, 2015). Calibration samples were analyzed using NREL Laboratory Analytical Procedures (Sluiter et al., 2010) and consisted of perennial cool season grasses as described in Payne et al., (2017), corn stover (*Zea mays* L.), *Miscanthus* × giganteus, sorghum (*Sorghum bicolor* (L.) Moench), switchgrass (*Panicum virgatum* L.), and rice straw (*Oryza sativa* L.). A summary of calibration and validation statistics is in Table S1.

Volatiles, carbon, ash, and nitrogen were also predicted using NIR spectra collected as described in the previous chemical composition section. PLS1 models were built to predict volatiles, carbon, ash, and nitrogen, and a summary of calibration and validation statistics is in Table S2. Calibrations included mixed perennial grasses—which included mixtures of little bluestem (*Schizachyrium scoparium*), intermediate wheatgrass (*Thinopyrum intermedium*), orchardgrass (*Dactylis glomerata*), pubescent wheatgrass (*Agropyron intermedium* var. trichophorum), smooth bromegrass (*bromus inermis*), tall fescue (*Schedonorus phoenix*), alfalfa (*Medicago*), *Lespedeza*, red clover (*Trifolium pratense*), white clover (*Trifolium repens*), and yellow sweetclover (*Melilotus officinalis*)—energycane (*Saccharum* hyb.), *Miscanthus* × *giganteus*, sorghum, switchgrass, willow (*Salix* spp.), and hybrid poplar (*Poplar* hyb.) samples. Calibration samples were analyzed for volatiles and ash using a LECO Thermogravimetric Analyzer (TGA) 701 (St. Joseph, MI, USA) following ASTM D 5142–09. Volatiles were determined by adding caps to crucibles after the samples were dried at 107°C and then ramping the temperature 50°C/min under 10 lpm of UHP N^2 until it reached 950°C where it was held for 9 min. To measure ash, caps were removed after the instrument cooled to 600°C. Then the instrument was heated at 13°C/min under 3.5 lpm of O_2 until it reached 750°C where it was held until the sample reached a constant weight. To determine carbon and nitrogen, samples were analyzed on a LECO TruSpec CHN Analyzer according to a modified ASTM D 5373–10 method (Flour and Plant Tissue Method) that uses a slightly different burn profile.

2.3 | Environmental variables

Precipitation, drought, and GDD were included in the PLS regressions because these variables have been previously demonstrated to affect biomass chemical attributes (Ong et al., 2016; Sanderson & Wolf, 1995). Each variable was calculated from the first frost-free day in spring until the first frost in fall as a representation of the growing season. In addition, these variables were calculated for the last 30 days before frost in the fall because it was hypothesized that the final days of the growing season would have an impact on the resulting biomass chemistry. This was based on previous research in which switchgrass responded well to moisture following drought (Barney et al., 2009). Weekly drought conditions for each county in the study were obtained from the University of Nebraska-Lincoln U.S. Drought Monitor (U.S. Drought Monitor, 2018). Severity of drought conditions are based on several models and measures, including the Palmer Drought Index, the Climate Prediction Center Soil Moisture Model, the U.S. Geological Survey Weekly Streamflow, the Standardized Precipitation Index, drought duration, and additional region-specific information. The U.S. Drought Monitor conditions are broken into five drought categories: abnormally dry (D0), moderate drought (D1), severe drought (D2), extreme drought (D3), and exceptional drought (D4). The weekly data from the U.S. Drought Monitor was a percent area in each county that was in each drought category (D0-D4). The Drought Severity and Coverage Index (DSCI)—developed by Adnan Akyuz at North Dakota

State University and implemented by the U.S. Drought Monitor—was used to calculate one value per county for each week (Equation 1) and the Accumulated Drought Severity and Coverage Index (ADSCI) was used to calculate a value for a county over a designated time period (2) (Akyuz, 2017). DSCI values can range from 0 to 500.

$$\mathrm{DSCI} = 1 * \mathrm{D0} + 2 * \mathrm{D1} + 3 * \mathrm{D2} + 4 * \mathrm{D3} + 5 * \mathrm{D4} \tag{1}$$

where D0 is abnormally dry and D4 is exceptional drought.

$$ADSCI = \sum\nolimits_{i=1}^{n} \mathrm{DSCI} \tag{2}$$

where n is weeks.

ADSCI was calculated for four different timeframes per year for each site—first frost free day to harvest, first frost-free day to first frost, 30 days before harvest, and 30 days before first frost. Note that the drought data were reported on a weekly basis, so the timeframes would start at the beginning of the week or end at the end of the week that included each of the days specified. According to NOAA, when temperatures drop below 2°C localized frost can occur, below 0ºC widespread frost with some freeze occurs, and below −2°C a hard freeze can happen (NOAA, 2020). In this study, frost was considered −2°C based on the temperature NOAA considers a hard freeze.

Precipitation and temperature data were obtained from weather stations near each site where switchgrass was grown (Station USW00094989, Ames Municipal Airport, IA; Station USC00304174, Ithaca Cornell University, NY, US; USW00093953, Muskogee Davis Field, OK, US; USC00390120, Andover number 2, SD, US; USC00441614, Chatham, VA, US). Precipitation was summed for four different time periods—first frost-free day to harvest, first frost-free day to first frost, 30 days before harvest, and 30 days before first frost. GDDs were calculated for two time periods—January 1 to harvest and first frost-free day to first frost—using Equation (3).

$$\Sigma \frac{\mathrm{Tmax} + \mathrm{Tmin}}{2} - \mathrm{T_{base}} \tag{3}$$

where T_{max} was the maximum daily temperature, T_{min} was the minimum daily temperature, $T_{base} = 12$°C (Kiniry et al., 2008), and if T_{max}+T_{min}/2 was less than 12°C then T_{max}+T_{min}/2 was set equal to T_{base} (12°C).

Soil cores were collected from three landscape positions in each plot—shoulder, backslope, footslope—at depths of 0 to 5, 5 to 15, and 15 to 30 cm as described previously in Hong et al. (2014). Soils were collected at different depths because soil properties can change over the soil depth profile. Soil samples were collected from Iowa in May 2009, New York in April 2008, Oklahoma in October 2008, South Dakota in May 2008, and in Virginia in March 2009. Soil data from each plot was summarized on a per location basis for analyses described below. Soil samples from each depth were analyzed for bulk density (g cm^{-3}), pH, and total soil nitrogen (%). Total soil C and nitrogen (TN) were analyzed by dry combustion using a TruSpec CHN analyzer (LECO Corporation, St. Joseph, MI). Soil bulk density was calculated using the core method (Blake & Hartge, 1986). Soil pH was determined using the pH meter (Thermo Scientific Orion, model-Orion Star A215). Soil drainage was categorized as good or poor according to Fike et al. (2017). National Commodity Crop Production Index (NCCPI) values were obtained from USDA-NRCS Soil Survey Geographic Database (SSURGO) for corn, soybeans (*Glycine max* (L.) Merr.), cotton (*Gossypium* spp.), small grains, and highest overall value (NRCS, 2008).

2.4 | Statistical analysis

Variance estimation for each chemical component was conducted using restricted maximum likelihood method (REML) mixed models in JMP 14.2.0 (SAS Institute, Inc., Cary, NC) to determine if there were any statistically significant differences in switchgrass chemistry resulting from location, harvest year, block, and interactions between factors. All locations and ecotypes were analyzed together in these REML mixed models. Nitrogen application rate was considered a fixed factor. Location, which includes cultivar differences, harvest year, block, and interactions between factors were considered random. Factors were considered significant if $p < 0.05$ (Wald p-value for random factors). Normality assumptions were assessed by reviewing histograms of residuals and normal quantile plots. Assumptions related to homogeneity of residuals were assessed by reviewing plots of residuals versus predicted values and O'Brien and Brown–Forsythe tests. Glucan and volatile data sets were reflect- and square root transformed (reflect = added one to the maximum value of the data set and then subtracted each value from this constant, followed with a square root transformation) and the ash data set was log10 transformed to meet the assumptions of normality and homogeneity required for analysis.

2.5 | Partial least squares models

Models were developed to understand relationships among the biomass chemical attributes and environmental and production variables to determine the primary variables impacting biomass chemistry and to predict these biomass chemical attributes using publicly available data sets of environmental variables. A PLS algorithm was selected because the various environmental variable representations used in this study are collinearly related (Figures S1 and S2). Biased regression approaches like PLS are well suited to handle this collinearity while still providing means to mathematically compare the factors using VIP scores. Partial least squares (PLS) models were developed in MATLAB R2017b ® (The Math Works, Natick, MA) using environmental and production factors to predict chemical composition (glucan, xylan, lignin, volatiles, fixed carbon, nitrogen, ash) and determine predictor variables with the most importance to the model. Upland switchgrass cultivars were combined into one data set, whereas the lowland switchgrass cultivar in Virginia was in a separate data set. Upland and lowland switchgrass have been separated in previous research on yield potential maps (Daly et al., 2018). The USDA plant hardiness zone ranges are different for these two switchgrass ecotypes (Daly et al., 2018). The intent of this design was to ensure the results would be more applicable when new cultivars are developed compared with models based on each cultivar individually. Fifty-eight environmental and production variables were used for upland models and included the following 15 variables: stand age, nitrogen application rate (three rates), dry biomass yield, drought (ADSCI calculated for four different timeframes), precipitation (summed for four different time periods), and GDD (summed for two different time periods). In addition, 43 soil and NCCPI variables were included for each location and are described in Table S3. Lowland models used 15 environmental and production variables including stand age, nitrogen application rate (three rates), dry biomass yield, drought (ADSCI calculated for four different timeframes), precipitation (summed for four different time periods), and GDD (summed for four different time periods). Predictor variables that were categorical—nitrogen application rate and soil drainage—were entered into the model as dummy variables (−1, 1). For example, for nitrogen application rate there were three categories, or levels—low (0 kg/ha), medium (56 kg/ha), and high (112 kg/ha)—and for each sample a 1 was entered for the level that was applied and a −1 was entered for each of the other two levels. Both predictor variables and response variables (chemical composition) were mean-centered and scaled to a standard deviation of 1. The SIMPLS algorithm was used and the number of factors to include in each model was determined based on balancing the bias/variance trade-off by minimizing the sum of the range scaled root-mean-square errors of calibration/cross validation (RMSEC/RMSECV) and normalized regression vectors (Kalivas & Palmer, 2014). A leave-multiple out cross validation was done where 20% of the data set was randomly selected and left out, and this was repeated over 20 iterations. Models were made for lowland and upland ecotypes of switchgrass separately. Lowland models included Virginia only. Variable importance in project (VIP) scores were used to compare the importance of each predictor variable in the PLS models. Predictor variables were considered important if their VIP score was greater than 0.8 and highly important if their VIP score was greater than 1, which are typical cutoffs used when discussing variable importance (Akarachantachote et al., 2014; Kuhn & Johnson, 2013).

3 | RESULTS AND DISCUSSION

3.1 | Chemical material attribute variability

Upland and lowland switchgrass chemical attributes varied within and across locations supporting the need to investigate potential sources of this variability. Chemical variability was larger for upland switchgrass because it included four field locations—Iowa, New York, Oklahoma, South Dakota—compared with lowland switchgrass that had one field location in Virginia. Glucan ranged from 28 to 37%, xylan from 18 to 24% and lignin from 16 to 21% for upland switchgrass (Figure 1). More limited variability existed for lowland switchgrass chemical composition with glucan ranging from 33 to 38%, xylan from 22 to 25%, and lignin from 19 to 22% (Figure 1). Harvest in Virginia was much later, which may have resulted in greater weathering perhaps partly contributing to the lower variability observed.

NIRS prediction model error (RMSEC) was 1.7% for glucan, 1.1% for xylan, and 1.1% for lignin (Table S1) helping to establish a minimum threshold range for meaningful variability necessary to determine if sample differences are within the error of the model. Ranges of chemical attributes for upland switchgrass were larger than the variability of the NIRS prediction model (Figure 1). Results for lowland switchgrass were analyzed but should be viewed with more caution because the ranges are narrower and closer to the method limits for meaningful variability. Ranges of variation for carbon, volatiles, nitrogen, and ash are larger than primary method analytical error and NIRS prediction model error (RMSEC); errors were 1.3% and 0.77% for volatiles, 0.23% and 0.58% for carbon, 0.04% and 0.10% for nitrogen, and 0.05% and 0.58% for ash, respectively (Figure 2, Table S2). The instrument error is based on acceptable or typical ranges of instrumental variability for analytical standards.

Upland switchgrass had a minimum of 72% volatiles and a maximum of 84% with most of the variation between location and within the Oklahoma field site (Figure 2a). Higher volatiles are related to increased fuel acidity following pyrolysis (Carpenter et al., 2014), faster burn rates in direct combustion (Jenkins et al., 1998), and decreased energy density of char from HTL (Onwudili et al., 2014). Carbon had location-to-location variation with an overall

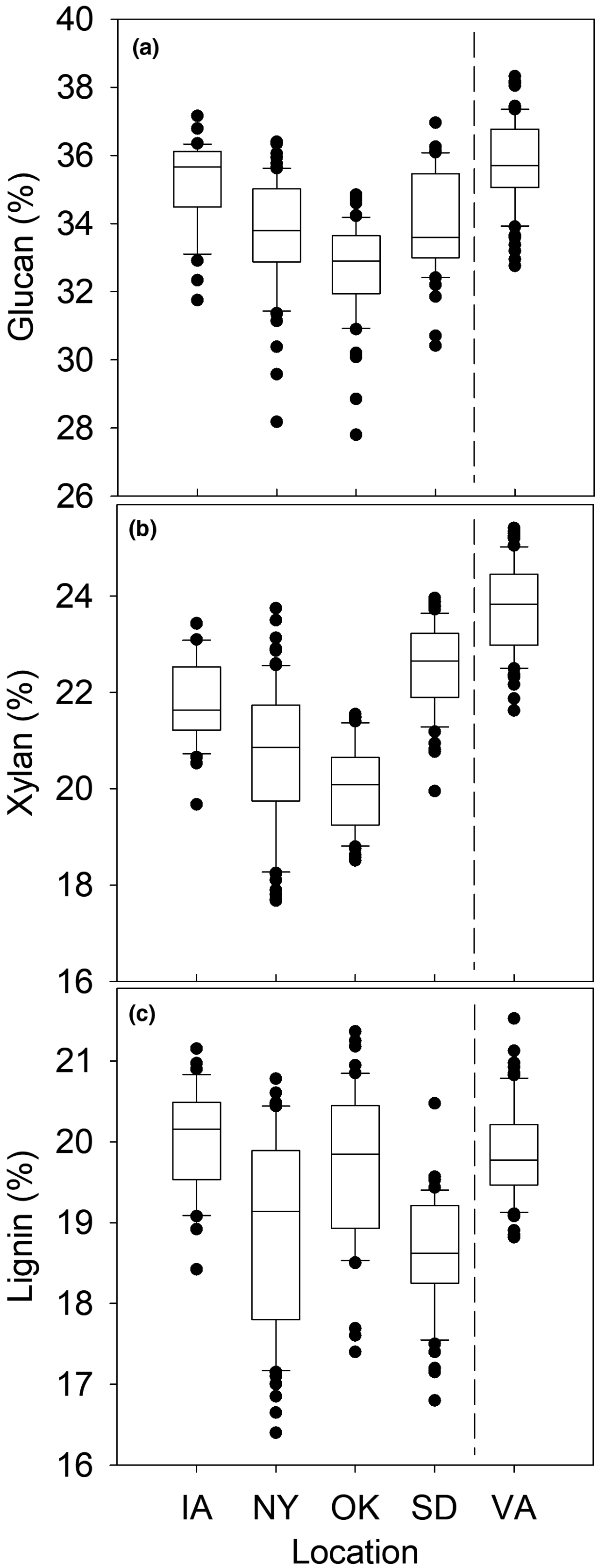

FIGURE 1 Variation in (a) glucan, (b) xylan, and (c) lignin concentration of switchgrass grown in five locations. Indicated by the dashed line, upland switchgrass was grown in Iowa, New York, Oklahoma, and South Dakota and lowland switchgrass was grown in Virginia

range of 46%–51% (Figure 2c). Lowland switchgrass had narrower ranges for volatiles and carbon, 3% and 2%, respectively. Nitrogen was 1% or less for all upland and lowland switchgrass similar to the range identified previously for 102 switchgrass samples (mean 0.8, standard deviation 0.7%) (Williams et al., 2016). When perennial plants are harvested after killing frost, concentrations of nitrogen and other mobile nutrients are often low because of nutrient translocation to the roots. Lower nitrogen concentration has been reported for switchgrass harvested near anthesis or after a killing frost compared with earlier in the growing season (Mulkey et al., 2006; Vogel et al., 2002). Ash concentration in Iowa, New York, and Virginia was between 2% and 6% (Figure 2b), close to physiological ash (Kenney et al., 2013). Ash was higher and more variable in Oklahoma (6%–12%) and South Dakota (5%–9%), perhaps reflecting contamination that can occur during field harvest. Samples from Oklahoma and South Dakota were collected after baling by coring the bales whereas the samples for Iowa, New York, and Virginia were taken from windrows prior to baling, likely explaining this difference since it has been observed that the baler can pick up debris and soil from the field.

3.2 | Nitrogen application rate, year, and location impacts

Overall, location/cultivar and year had more of an impact on feedstock quality than fertility management. Location/cultivar, nitrogen fertilizer application rate, and year explained over 85% of the variation when all locations were considered together—based on the adjusted R^2—for all switchgrass chemical attributes except nitrogen (adj R^2 = 79%) and glucan (adj R^2 = 65%; Table 2). Significant ($p \le 0.03$) location/cultivar × year interaction for all chemical attributes indicates the importance of environment as an influential variable. However, location and environmental effects are not completely distinguishable because different cultivars were grown at all locations except for Iowa and New York where Cave-In-Rock was planted (Table 1). Nitrogen application rate was less influential overall but significantly affected xylan, carbon, and nitrogen; glucan was significantly impacted by a nitrogen × year interaction (Table 2). These trends agreed with the results of Hong et al. (2014) who reported nitrogen application rate increased nitrogen and reduced hemicellulose concentrations in switchgrass; moreover, as with our findings, location and year had stronger effects on feedstock quality than fertility management. Variance

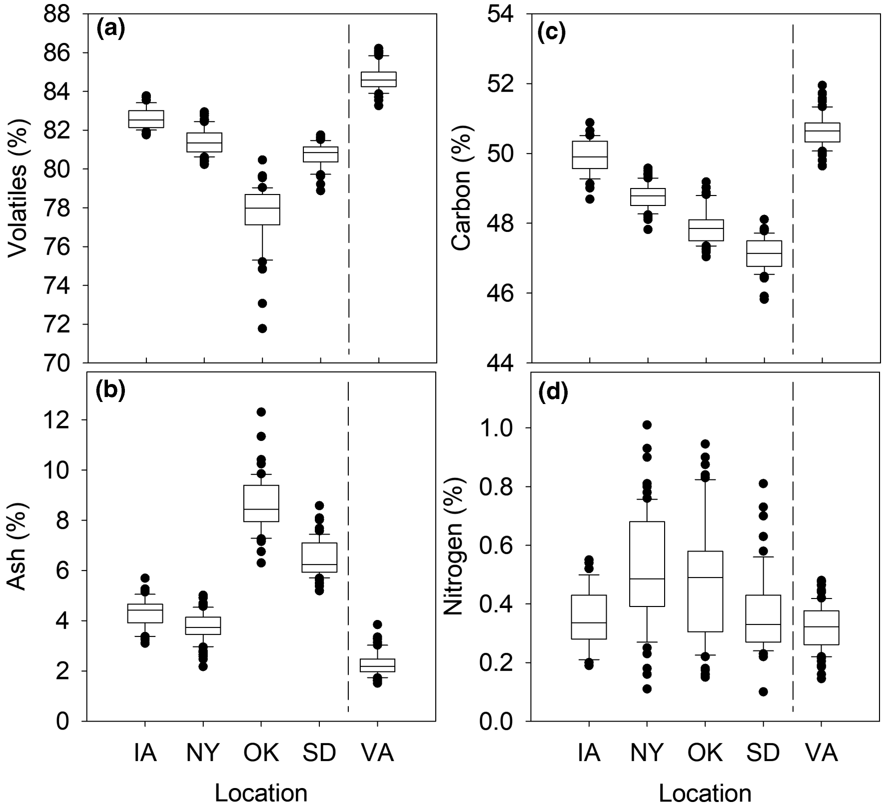

FIGURE 2 Variation in (a) volatiles, (b) ash, (c) carbon, and (d) nitrogen concentration of switchgrass from five locations. Indicated by the dashed line, upland switchgrass was grown in Iowa, New York, Oklahoma, and South Dakota and lowland switchgrass was grown in Virginia. Iowa, New York, and Virginia samples were collected from windrows whereas Oklahoma and South Dakota samples were collected by coring bales

TABLE 2 Restricted maximum likelihood variance estimation p-values for seven chemical attributes and three factors—location/cultivar (LC), nitrogen rate (N), year (Y)

Chemical component	LC	N	Y	Block	LC × N	LC × Y	N × Y	LC × N × Y	R^2 adj.	RMSE
Glucan	0.23	0.96	0.37	0.43	0.12	**0.02**	**0.01**	0.37	0.65	0.24
Xylan	0.18	**0.00**	0.64	0.55	0.28	**0.01**	0.36	0.54	0.88	0.64
Lignin	0.41	0.97	0.91	0.53	0.29	**0.01**	0.91	0.15	0.87	0.41
Volatiles	0.16	0.97	0.66	0.64	0.12	**0.01**	0.37	0.80	0.96	0.12
Ash	0.16	0.74	0.47	0.42	0.18	**0.03**	0.67	0.96	0.95	0.05
Carbon	0.16	**0.02**	0.32	0.79	0.22	**0.01**	0.80	0.71	0.96	0.30
Nitrogen	0.37	**0.00**	0.74	0.37	0.12	**0.02**	0.61	0.55	0.79	0.09

Note: Significant ($p < 0.05$) are bolded. This analysis includes both upland and lowland ecotypes.

analysis results support additional analyses to determine the specific environmental variables underlying the location/cultivar × year interaction, and to assess how much variation can be accounted for without including factors like cultivar for upland switchgrass.

3.3 | Relationships between production and environmental factors and chemical attributes

Using PLS regressions, production variables and environmental conditions that occurred during the field trials were used to explain switchgrass chemical attribute variation. This is the first study to use this type of modeling approach to successfully build relationships of this type to the authors' knowledge. These relationships are critical for both understanding the importance of key sources of variability on biomass chemical attributes and for predicting attribute ranges of variability that may occur over time and in different locations. Table 3 displays the PLS regression results for the seven chemical attributes for upland (IA, NY, OK, SD) and lowland (VA) switchgrass separately. These regressions included explanatory production variables of stand age, nitrogen application rate, and dry biomass yield and explanatory environmental

TABLE 3 Partial least square model results for upland and lowland switchgrass

Cultivar type	Chemical component	LV	% X variance explained	R^2 Cal.	R^2 CV	RMSEC	RMSECV
Upland	Glucan	17	100	0.58	0.44	0.64	0.73
	Xylan	17	100	0.78	0.74	0.47	0.52
	Lignin	17	100	0.80	0.78	0.44	0.48
	Volatiles	15	100	0.89	0.86	0.33	0.39
	Ash	17	100	0.92	0.90	0.28	0.32
	Carbon	17	100	0.92	0.90	0.28	0.31
	Nitrogen	17	100	0.72	0.67	0.53	0.58
Lowland	Glucan	4	74	0.66	0.60	0.57	0.62
	Xylan	5	85	0.55	0.54	0.67	0.71
	Lignin	4	76	0.64	0.51	0.60	0.67
	Volatiles	8	100	0.67	0.61	0.56	0.61
	Ash	8	100	0.68	0.61	0.56	0.67
	Carbon	5	83	0.65	0.62	0.58	0.67
	Nitrogen	4	78	0.56	0.51	0.66	0.71

Note: Results, except for latent variable (LV), represent the mean results from a 20-iteration cross validation using a randomly selected 20% cross validation sample set for each iteration.

Abbreviations: Cal., calibration; CV, cross validation; RMSEC, root mean square error of calibration; RMSECV, root mean square error of cross validation.

variables of drought, precipitation, GDDs, soil properties, and NCCPI (Tables 4 and 5). Drought, precipitation, and GDD in Tables 4 and 5 were numerically expressed in multiple ways to better capture the environmental conditions, particularly if different chemical attributes were sensitive to environmental conditions at different times in the growing season. Selection of the optimal expression of each variable for individual chemical attributes is beyond the scope of this research and would be the subject of future work.

Environmental and production variables could explain 72% to 92% of the variability in upland switchgrass chemical attributes, except for glucan (R^2 cal. = 0.58; Table 3). Measured values versus predicted chemical attributes from regressions show that most regressions were close to the line of equality with slight overprediction on the lower values and underprediction for the upper range (Figure 3). Most chemical attributes fell very close to the line of equality; glucan and nitrogen deviated the most from the line of equality and both attributes had less variation explained by the PLS regressions possibly because of similar medians across sites or sample outliers (Figures 1–3). For specific year-location combinations, groupings can be seen where the chemical data predictions are similar across all of the samples. This is especially obvious in the upland lignin model in Figure 3c but can be seen at varying levels in the other chemical attribute predictions. These trends indicate that the plot-to-plot factors available for this work, dry biomass primarily, were not sufficient for predicting these chemical properties. More investigation is necessary that includes other factors like soil characteristics and slope at the plot level to accurately predict biomass chemical attributes. Additionally, this study was not able to pull apart the difference between location and cultivar. These models could potentially improve if cultivar was considered. There are potential interactions between the plot variables, soil characteristics, and the cultivars themselves.

Volatiles, carbon, and ash data for upland switchgrass clustered by location (Figures 3 and 4). This is likely a result of a complex interaction of factors including cultivar and the environmental conditions at each location and across years. Stand age is another important factor for perennial crop chemical attributes, as biomass yield, which is related to plant size and structures like leaf-to-stem ratios, typically increases during the first 3 years of production (Hong et al., 2014; Parrish & Wolf, 1992). Iowa may cluster separately from the other locations because only three growing seasons from Iowa were part of this study, whereas the other locations had 5–6 years of samples (Table 1). Samples also clustered by year for glucan, lignin, and volatiles even though year was not a variable in the models (Figure S3).

Less of the chemical variability was explained for lowland switchgrass (55% to 68%) compared with upland switchgrass (Table 3) likely a result of the smaller sample set. In addition, these models did not include the added benefits of soil/landscape explanatory variables as only

TABLE 4 Variable importance of projection (VIP) scores from upland PLS models for each environmental or production variable

	Glucan	Xylan	Lignin	Volatiles	Ash	Carbon	Nitrogen
Stand age (yr)	1.5	0.8	1.1	0.7	0.6	1.0	2.2
0 Nitrogen application rate (kg/ha)	0.5	2.0	0.5	0.4	0.3	0.7	2.1
56 Nitrogen application rate (kg/ha)	0.3	0.2	0.2	0.1	0.1	0.1	0.5
112 Nitrogen application rate (kg/ha)	0.4	2.1	0.4	0.6	0.4	0.8	2.6
Dry biomass yield (Mg/ha)	2.9	0.8	0.7	0.9	0.8	1.2	1.5
ADSCI-first frost-free day to harvest	1.1	1.1	1.9	0.8	0.8	0.8	1.7
ADSCI-first frost-free day to first frost	1.0	0.9	1.5	0.8	0.8	0.7	1.5
ADSCI—30 days before harvest	1.2	0.9	1.0	1.4	0.8	1.1	1.3
ADSCI—30 days before first frost	0.9	0.9	1.3	0.8	0.5	1.1	1.3
Precip.-first frost-free day to harvest	2.4	1.6	2.4	1.4	0.8	0.8	1.9
Precip.-first to last frost-free day	2.5	1.4	1.7	1.4	0.9	0.6	1.4
Precip.—30 days before harvest	1.6	0.8	1.7	1.0	1.0	0.6	0.8
Precip.—30 days before first frost	0.8	0.9	1.3	0.7	0.5	1.0	0.9
GDD-January 1 to harvest	1.5	1.8	3.3	1.6	1.5	0.8	1.7
GDD-first to last frost-free day	1.4	1.7	3.0	1.6	1.5	0.7	1.5
Soil drainage	0/2	2/2	2/2	0/2	0/2	2/2	0/2
Total soil nitrogen	5/12	1/12	1/12	9/12	11/12	11/12	1/12
Soil bulk density	1/12	8/12	3/12	3/12	8/12	10/12	1/12
Soil pH	8/12	12/12	0/12	7/12	3/12	5/12	4/12
NCCPI	4/5	1/5	4/5	2/5	1/5	4/5	4/5

Note: Yellow values are 0.8 or greater, and green values are 1 or greater. For soil variables and NCCPI values are the number of variables out of the total in that category that had VIP scores greater than 0.8 (see Table S3 for soil/NCCPI VIP scores).

Abbreviations: ADSCI, accumulated drought severity and coverage index; GDD, growing degree days, NCCPI, National Commodity Crop Production Index; precip., precipitation.

one location was considered. Future research that includes multiple field locations for lowland switchgrass would allow more robust regression development. R^2 and RMSE were similar for the regression calibrations and cross validations indicating adequate model robustness; however, regressions overpredicted lowland feedstock constituent concentrations in the low range and underpredicted their concentration in the high range of the data similar to upland switchgrass models (Figure 5). Samples clearly clustered by year for all chemical attributes except ash, which clustered by year primarily only in 2009 (Figures 4 and 5). This was not surprising given the year-to-year variation in environmental conditions, length of growing season, stand age, and dry biomass yield (Figure 5). These results necessitated further assessment of the environmental and production variables that had the largest impact on the regressions.

VIP scores were calculated to quantify the importance of each environmental and production variable on each chemical material attribute. VIP scores for upland switchgrass indicated that a multitude of production and environmental variables impacted the chemical attributes of switchgrass, with VIP scores greater than 1 for every category of variable: stand age, nitrogen application rate,

TABLE 5 Variable importance of projection (VIP) scores from lowland PLS models for each environmental or production variable

	Glucan	Xylan	Lignin	Volatiles	Ash	Carbon	Nitrogen
Stand age (yr)	1.4	1.2	1.8	1.5	1.5	1.3	1.6
0 Nitrogen application rate (kg/ha)	0.3	1.4	0.6	0.4	0.3	0.3	0.6
56 Nitrogen application rate (kg/ha)	0.4	0.3	0.5	0.6	0.9	0.8	0.5
112 Nitrogen application rate (kg/ha)	0.2	1.6	0.2	0.5	0.6	0.6	1.0
Dry biomass yield (Mg/ha)	0.8	0.6	0.8	1.4	1.1	0.7	0.9
ADSCI-first frost-free day to harvest	0.2	0.7	0.8	0.8	0.7	0.6	0.7
ADSCI-first frost-free day to first frost	0.6	0.5	1.1	0.4	0.3	0.9	0.4
ADSCI—30 days before harvest	0.6	0.8	0.5	1.0	0.9	0.6	1.1
ADSCI—30 days before first frost	1.7	0.8	1.1	0.3	0.8	1.9	0.3
Precip.-first frost-free day to harvest	0.7	1.3	1.1	1.8	1.0	0.9	1.2
Precip.-first to last frost-free day	1.3	1.6	1.4	1.3	1.6	0.9	1.5
Precip.—30 days before to harvest	1.2	1.0	1.0	1.3	1.5	0.7	1.6
Precip.—30 days before first frost	2.0	0.9	1.0	1.1	1.4	1.8	1.2
GDD-January 1 to harvest	0.6	0.5	1.0	0.5	0.3	0.8	0.3
GDD-first to last frost-free day	0.7	0.5	1.1	0.4	0.3	0.9	0.4

Note: Yellow values are 0.8 or greater, and green values are 1 or greater.

Abbreviations: ADSCI, accumulated drought severity and coverage index; GDD, growing degree days; precip., precipitation.

dry biomass yield, drought, precipitation, GDD, soils, and NCCPI (Table 4). Given that lowland switchgrass was grown at only one location, it served as a case study to show the effects of year-to-year environmental variability coupled with the production factors of nitrogen application rate and stand age. VIP scores for lowland switchgrass indicate that while each category of variable was important, stand age and precipitation were particularly important for all chemical attributes (VIP>1; Table 5). The VIP results highlight the complexity of plant responses to growing conditions and the need to carefully select the combination of factors that best represents this when trying to explain as much variability as possible in a feedstock's chemical attributes.

Production and field management factors must be considered when trying to explain the variability in chemical attributes of switchgrass. Therefore, stand age (i.e., the number of years since planting) and dry biomass yield were selected for inclusion in this study; these variables were important likely because they are related to plant structure and size, which affects leaf-to-stem ratios and lignocellulosic concentrations. Switchgrass plant size and yield typically increase with stand maturity, which usually is reached in year 3; yields in subsequent years can vary but often remain relatively constant or decline (Hong et al., 2014; Lee et al., 2018; Parrish & Wolf, 1992). Further, some research has correlated increased tiller size from year 1 to year 2 to increases in cellulose and hemicellulose, but lignin did not change (Hong et al., 2014); however, this trend was not seen in other studies (Lemus et al., 2002).

Soil fertility is an important management factor included in many field trials, yet its influence on biomass yields and chemical quality is not always straightforward and can be complicated by factors such as harvest management and land use history. In the PLS regression analysis, nitrogen application rate impacted only a few chemical attributes—mainly xylan, carbon, and nitrogen (VIP>0.8; Tables 4 and 5)—as identified in the REML variance analysis (Table 2). A previous meta-analysis found similar

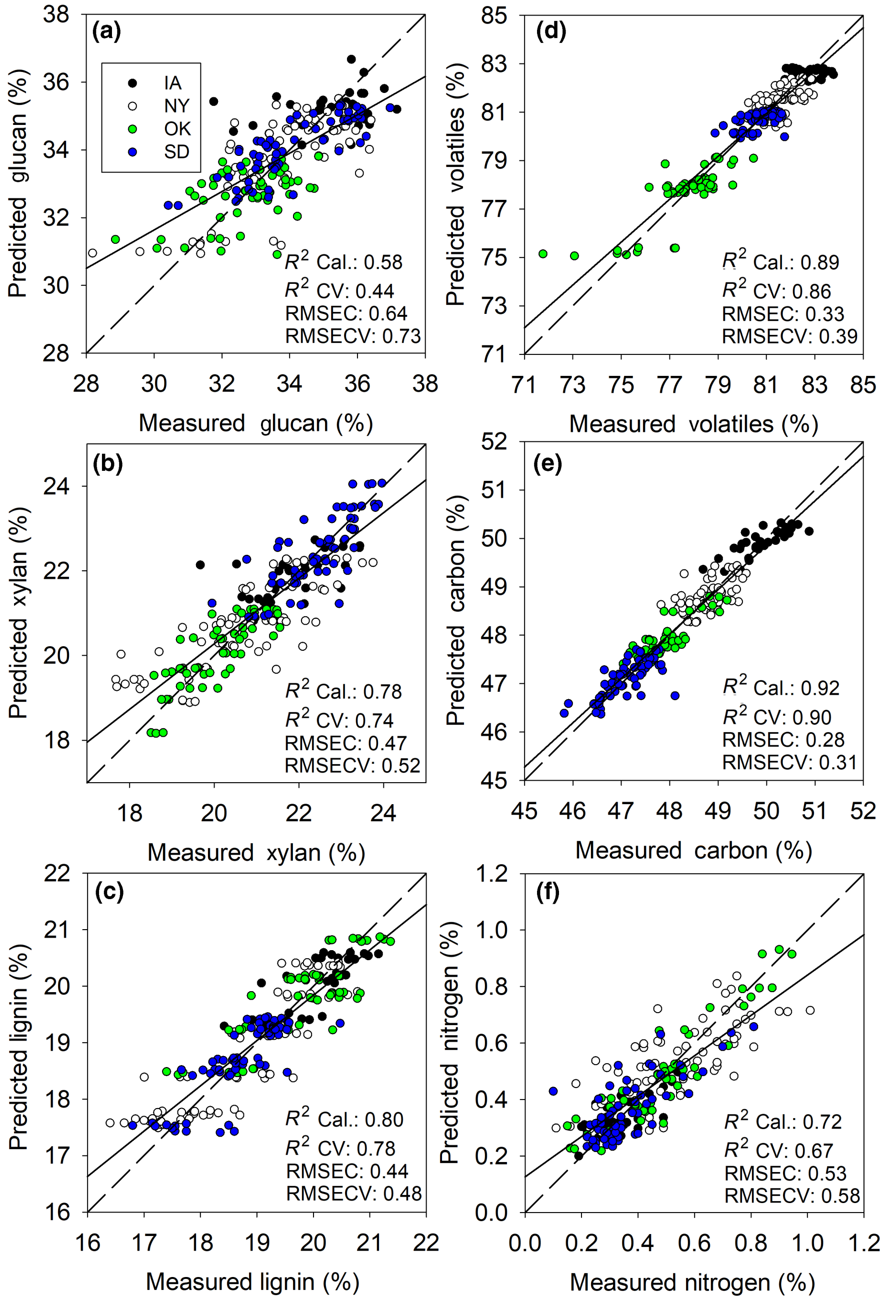

FIGURE 3 Measured glucan (a), xylan (b), lignin (c), volatiles (d), carbon (e), and nitrogen (f) versus these chemical attributes predicted using environmental and production variables for upland switchgrass cultivars in Iowa, New York, Oklahoma, and South Dakota. Solid line is the regression and the dashed line is the line of equality (slope=1, intercept=0)

patterns of increasing nitrogen application rates decreasing hemicellulose but not cellulose concentrations (Liu et al., 2016). In switchgrass and switchgrass-dominated grasslands, feedstock nitrogen concentrations typically increased with increasing nitrogen application (Hong et al., 2014; Kering et al., 2013; Mulkey et al., 2006).

Switchgrass grown in a field setting is susceptible to a myriad of environmental conditions known to impact biomass chemical attributes. Precipitation, drought, and GDD had VIP scores greater than 0.8 for upland switchgrass chemical attributes. In contrast to upland switchgrass, precipitation had a particularly large effect on lowland switchgrass chemical attributes, whereas drought and GDD had less of an impact on overall chemical attributes. In 2012, there was a nationwide drought in the United States, and during that time the accumulated drought severity and coverage index (ADSCI) for Virginia was 1200, but the maximum drought extent for the upland switchgrass was more than 50% higher in Iowa (2000) and Oklahoma (1900) helping explain why drought variables may have been more influential in the upland switchgrass PLS regressions. Plants may accumulate solutes (e.g., non-structural sugars and osmolytes), during drought and low precipitation to maintain essential functions like turgor pressure and then on a percent dry mass basis structural sugars would proportionally also change (Chaves et al., 2003; Ong et al., 2016). Neither a plant's stunting by nor its recovery from past environmental stressors (or their combined effects) may be captured by calculated drought indices, which may explain the lower R^2 calculated for upland switchgrass glucan concentrations (Table 3). Similar to drought indices, the spread of GDD in the PLS regression was also much larger for upland switchgrass because samples were grown in multiple locations. The range of GDD from first to last frost was 1351–1741 GDD for lowland switchgrass in Virginia; in comparison, upland switchgrass had a minimum of 742 GDD in New York in 2009 and 2643 GDD in Oklahoma in 2012. If future work is focused only on explaining the most variability possible with optimized predictions, then data sets can include all environmental data available. E.g., daily precipitation could be used rather than aggregating precipitation over a given period. This study aimed to understand sources of variability, which necessitated some level of data aggregation. In addition, one of the challenges with switchgrass is that its growth may also be impacted by dormant season precipitation that recharges the soil water column. Future research should address the combined effects of moisture throughout the soil column, evapotranspiration, plant development stage(s), and the timing, length, and degree of stress on plant growth and physiology.

Soil samples were collected and analyzed once at the beginning of the study at each field site; therefore, soil data was included in the upland switchgrass analysis only, since upland switchgrass was planted at multiple locations. All soil factors—drainage, bulk density, and pH—along with NCCPI had VIP scores greater than 0.8; however, VIP scores greater than 0.8 or 1 varied per switchgrass chemical attribute (Table 4 and Table S3). For example, glucan and xylan had VIP scores greater than 0.8 for bulk density, pH, and NCCPI but lignin was not strongly related to pH (Table S3). The relationship between plant chemistry and soil pH (whether low or high) could reflect the effect of this factor on the ability of plants to absorb nutrients and supporting growth. Similarly, NCCPI values indicate productivity level of the land. The results generally closely align with differences between locations because this study did not capture within location variation in soils. Soil properties can be spatially and temporally heterogeneous and measuring subtle spatial and temporal changes can be cost prohibitive and challenging. Future data sets that include additional soil information would be valuable.

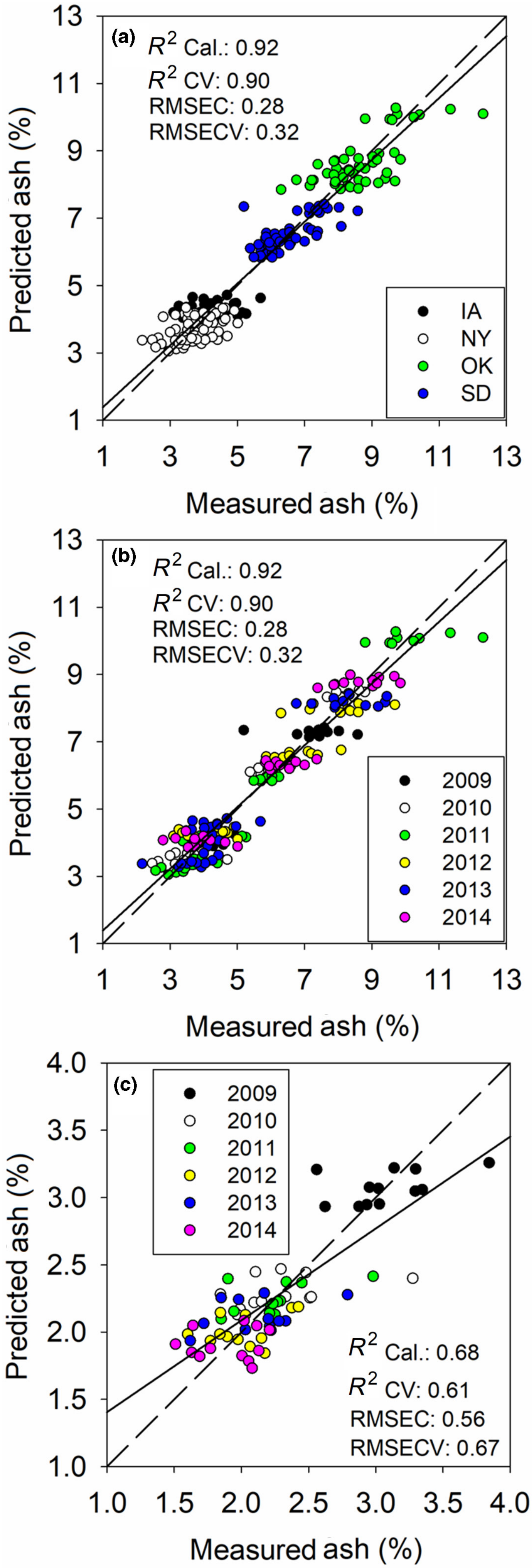

FIGURE 4 Measured ash versus ash predicted using environmental and production variables for upland switchgrass cultivars by location (a) and year (b) and for a lowland switchgrass cultivar by year (c). Solid line is the regression and the dashed line is the line of equality (slope=1, intercept=0)

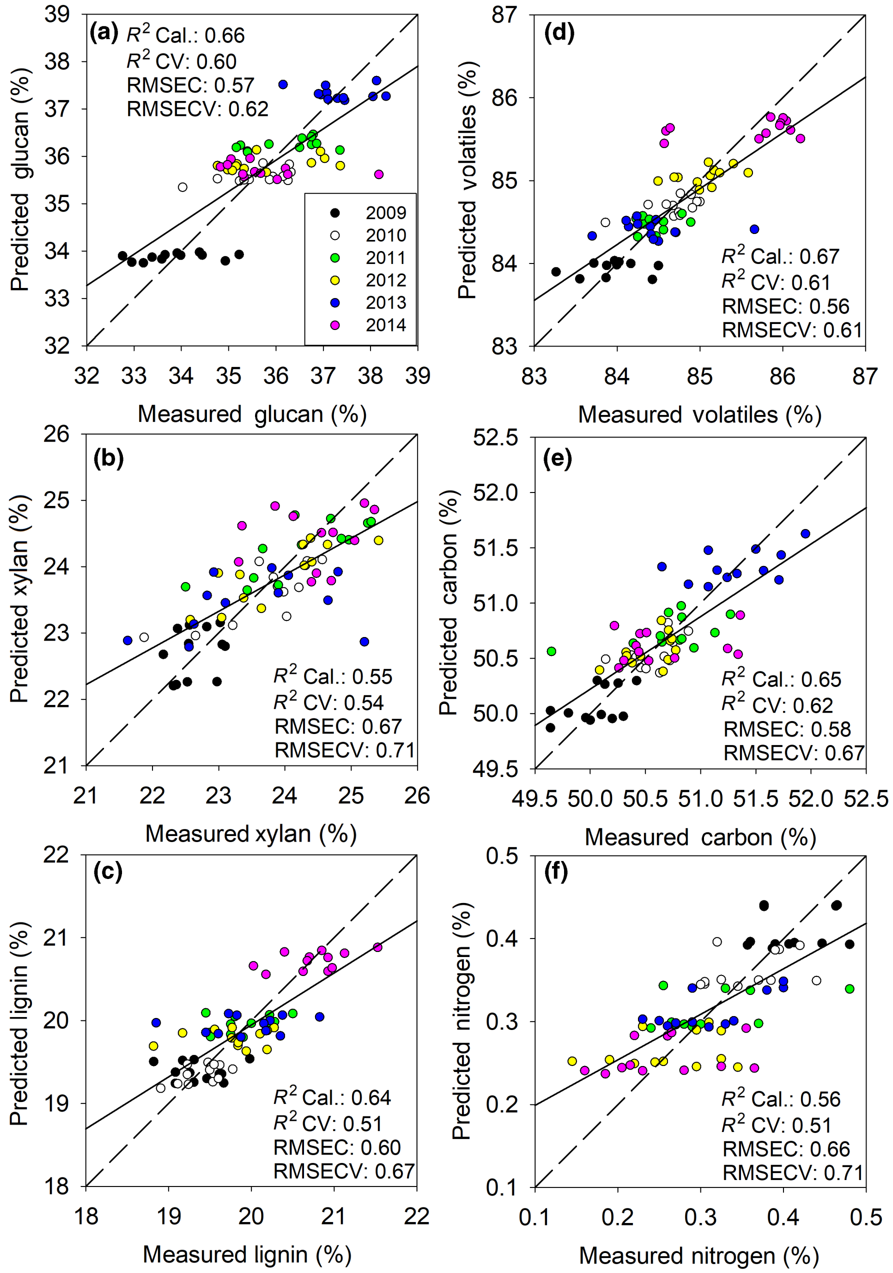

FIGURE 5 Measured glucan (a), xylan (b), lignin (c), volatiles (d), carbon (e), and nitrogen (f) versus these chemical attributes predicted using environmental and production variables for a lowland switchgrass cultivar from 2009 to 2014. Solid line is the regression, and the dashed line is the line of equality (slope=1, intercept=0)

4 | CONCLUSION

This study demonstrates a methodology for analyzing the complex plant response to field conditions that leads to the large ranges of biomass quality challenging downstream feedstock users. The successful building of relationships that link environmental and production variables to chemical attributes in this study allows for the prediction of spatial and temporal variation necessary to understand and mitigate risk for using heterogeneous biomass resources in the bioenergy and bioproducts industry. This study shows that PLS regression can be used to help understand the impact of these explanatory variables. Due to the complexity of interactions between the explanatory variables and chemical attributes, it is not possible to determine which explanatory variables with similar VIP scores are causing the change in plant chemistry. For example, for upland switchgrass locations, many soil properties were highly correlated with each other (Figure S1); in the lowland switchgrass location, precipitation was negatively correlated with dry biomass yield and drought (Figure S2). In many cases, complex interactions impact feedstock chemistry, and experiments will have to be specifically designed to understand these relationships, which is beyond the scope of this paper. This research, and the identified environmental and production variables, supports future work using the relationships in a predictive way to determine chemical attributes geospatially and temporally using publicly available databases. This capability would provide a state-of-the-art tool for predicting and understanding variability in chemical attributes for targeted biomass resources.

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CONFLICT OF INTEREST

The authors have no relevant affiliations or financial involvement with any organization or entity with a financial interest in or financial conflict with the subject matter or materials discussed in the manuscript apart from those disclosed. No writing assistance was used in the production of this manuscript.

DATA AVAILABILITY STATEMENT

Chemical composition data and metadata presented are available in the Bioenergy Feedstock Library (https://bioenergylibrary.inl.gov/data/dataset.aspx?id=1002).

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