Net Ecosystem Carbon Dioxide Exchange of Dedicated Bioenergy Feedstocks: Switchgrass and
High Biomass Sorghum

Pradeep Wagle^{1†}, Vijaya Gopal Kakani^{*1} and Raymond L. Huhnke²

¹Department of Plant and Soil Sciences, Oklahoma State University, 368 Ag Hall, Stillwater, OK
74078, USA

²Biosystems and Agricultural Engineering, Oklahoma State University, 223 Ag Hall, Stillwater,
OK 74078, USA

†Current address:

Pradeep Wagle
Center for Spatial Analysis
2100 SRTC
University of Oklahoma
Norman, OK 73019
Tel: 405-325-5568
Email: pradeep.wagle@ou.edu

*To whom correspondence should be addressed:

Vijaya Gopal Kakani
Department of Plant and Soil Sciences
368 AG Hall
Oklahoma State University
Stillwater, OK 74078
Tel: 405-744-4046
Fax: 405-744-0354
Email: v.g.kakani@okstate.edu

ABSTRACT

As switchgrass (*Panicum virgatum* L.) and high biomass sorghum (*Sorghum bicolor* L. Moench) acreages are expanding for cellulosic biofuels, it is critical to improve understanding of carbon dynamics of these two potential bioenergy crops. Eddy flux measurements from co-located switchgrass and high biomass sorghum fields during the 2012 and 2013 growing seasons were analyzed to quantify and compare net ecosystem CO₂ exchange (NEE) between two species. Monthly ensemble averaged NEE reached seasonal peak values of -36.9 ± 1.78 and -35.9 ± 2.32 $\mu\text{mol m}^{-2} \text{s}^{-1}$ in switchgrass and sorghum, respectively. Similar magnitudes of NEE (-10 to -11 $\text{g C m}^{-2} \text{d}^{-1}$), gross primary production (GPP, 19 - 20 $\text{g C m}^{-2} \text{d}^{-1}$) and ecosystem respiration (ER, 10 - 12 $\text{g C m}^{-2} \text{d}^{-1}$) were observed in both ecosystems. Similarly, carbon fluxes of both ecosystems had similar response to air temperature and vapor pressure deficit (VPD). Carbon fluxes exhibited an optimum temperature of slightly over 30 °C and decreased markedly beyond 35 °C. The NEE decreased markedly at higher VPD (> 3 kPa) because of the stomatal closure control of photosynthesis. The switchgrass field was a larger carbon sink, with a cumulative seasonal carbon uptake of -406 ± 24 to -490 ± 59 g C m^{-2} compared to -261 ± 48 to -330 ± 45 g C m^{-2} by the sorghum field. The switchgrass stand was a net carbon sink for four to five months (April/May-August), while sorghum appeared to be a net carbon sink for only three months (June-August). Our results imply that the difference in carbon sink strength between the two species was driven mainly by the length of the growing season.

Keywords: biofuels; eddy covariance; high biomass sorghum; net ecosystem exchange; seasonal variation; switchgrass

1. Introduction

United States of America has one-third of the world's automobiles (230 million) and uses about 25% of the world's oil (NBAP, <http://www1.eere.energy.gov/biomass/pdfs/nbap.pdf>, accessed April 11, 2013). According to the projection of the U.S. Energy Information Administration (EIA), the reliance on foreign oil will increase 30% by 2030 and the transport sector's greenhouse gas emissions will rise by 40% (Annual Energy Outlook, 2007, [ftp://ftp.eia.doe.gov/forecasting/0383\(2007\).pdf](ftp://ftp.eia.doe.gov/forecasting/0383(2007).pdf), accessed April 11, 2013). The demand and cost of energy are increasing while oil and gas reserves are declining (Sorrell et al., 2010). Moreover, the concentration of atmospheric CO₂ has increased substantially since the beginning of the Industrial Revolution. Most of the released CO₂ into the atmosphere is a result of burning fossil fuels (National Research Council, 2010). It is, therefore, necessary to produce alternative fuels from renewable sources to supplement transportation fuel requirement and to curb CO₂ emissions to the atmosphere. To expand current ethanol production from sugar/starch, alternate feedstocks sources are required. The U.S. has capability of producing about 1.3 billion dry tons of biomass each year (Perlack et al., 2005). Even though the biomass available consists of many different species, switchgrass (*Panicum virgatum* L.) and high biomass sorghum (hereafter referred to as sorghum) (*Sorghum bicolor* L. Moench) are two major dedicated cellulosic feedstocks (USDA, 2010).

The Energy Information Agency website (<http://www.eia.gov>) reports that biomass energy consumption has increased by 60% from 2002 to 2013. In 2013, renewable energy contributed to about 9.3% of current energy requirements in USA and 50% of this renewable energy is from biomass sources. This biomass energy translates to about 4614 trillion Btu's from biomass with about 2000 trillion Btu's towards biofuels. This growth is mainly due to increased consumption

of biomass to produce biofuels, mainly ethanol blended with gasoline. Currently, corn (*Zea mays* L.) is the major feedstock for producing almost all ethanol produced in USA. However, cellulosic biofuel plants are making inroads with an existing capacity of 67.4 MMgy with another 129 MMgy proposed. The existing production capacity uses corn stover, corn cobs, switchgrass, and municipal solid waste. Through the USDA Biomass Crop Assistance Program (FSA, 2013), a total of about 20,000 ha have been planted to dedicated bioenergy crops such as switchgrass, miscanthus, and woody species. However, the production of energy crops, including switchgrass and sorghum, is expected to grow as most of the proposed ethanol plants will use energy crops for biofuel production and also as new pathways for sorghum biofuel production are approved by U.S. Environmental Protection Agency.

The benefits of dedicated energy crops are not only confined to transportation fuels, they also impact greenhouse gas emissions, soil erodability, soil carbon, microbial community changes, in essence impact ecosystem services. A recent study by Meehan et al. (2013) has demonstrated that integration of energy crops into agricultural landscapes promotes sustainability and they foster multiple ecosystem services (below ground carbon sequestration, pollinator abundance, biocontrol potential) and mitigate ecosystem disservices (e.g. phosphorous pollution, nitrous oxide emissions). The benefits to ecosystem services are region dependent. Evers et al. (2013) demonstrated that dedicated energy crops such as perennial warm-season grasses, after 4-5 years of management, can reduce the soil susceptibility to wind erosion but may not significantly increase soil organic carbon concentration in short term. Another ecosystem service of bioenergy crops in agroecosystems is in the area of soil microbial activity. Hargreaves and Hofmockel (2014) have demonstrated that having perennial crops such as switchgrass can affect the physiological capacity of microbial communities allowing for greater nitrogen retention and

greater rates of decomposition that can lead to reduced nitrous oxide emissions and increased carbon sequestration.

The North American Carbon Program Science Plan (Wofsy and Harriss, 2002) emphasized that it is necessary to quantify carbon sink of the North America. In recent years, direct measurements of net ecosystem CO₂ exchange (NEE) have increased in a variety of ecosystems. Long-term eddy covariance monitoring networks such as AmeriFlux and EUROFLUX have been established to measure NEE across a range of land-use categories; and data from several ecosystems are available for scientific communities. However, very few studies on source-sink dynamics of young switchgrass stands have been reported (Skinner and Adler, 2010; Wagle and Kakani, 2014c; Zeri et al., 2011). These studies reported a consistent result that switchgrass stands act as sinks of carbon for at least the first few years of stand establishment if the field is not harvested or a small quantity of biomass is removed. However, these studies indicated that major removal of biomass could encourage the stand to act as a source of carbon when accounting for carbon loss from biomass harvest. To our understanding, no source-sink dynamics of sorghum have been reported. Here, we compare the magnitude and seasonality of NEE and its two components, gross primary production (GPP) and ecosystem respiration (ER), between co-located annual sorghum and perennial switchgrass during the 2012 and 2013 growing seasons. This comparative study not only provides better understanding of the minimally studied source-sink dynamics of switchgrass and sorghum, it also provides greater insight on how these two ecosystems respond to the same climatic conditions. This study has great importance as the southern Great Plains of the U.S. will contain large stands of the cellulosic feedstocks in the near future (Downing et al., 2011).

2. Material and methods

2.1. Site description

Eddy covariance measurements were performed over co-located switchgrass (*cv.* Alamo) and sorghum (*cv.* ES 5200) fields (eight hectares each) at the South Central Research Station, Chickasha, OK (latitude: 35.04°N, longitude: 97.91°W, and elevation: 330 m above sea level). The site has a deep and well-drained soil, formed from weathered loamy alluvium. The predominant soil series is Dale silt loam (a fine-silty, mixed, superactive, thermic Pachic Haplustoll). Switchgrass stand was established in spring 2010 and sorghum was planted around mid-May each year. Prior to switchgrass greening and sorghum planting, herbicides were applied: 2.3 L ha⁻¹ of glyphosate + 1.2 L ha⁻¹ LV6 + 2.5 ml L⁻¹ squire in the switchgrass field and 2.3 L ha⁻¹ of crop oil + 1.7 L ha⁻¹ Metolchlor + 1.1 kg ha⁻¹ a.i. Atrazine in the sorghum field. Every year, urea and diammonium phosphate were applied to provide 75 kg N ha⁻¹ for switchgrass in April and 112 kg N ha⁻¹ for sorghum in May along with 39 kg P ha⁻¹ for each.

2.2. Micrometeorological and biometric measurements

CO₂ fluxes from co-located switchgrass and sorghum fields were measured using the eddy covariance technique, equipped with a three-dimensional sonic anemometer (Model CSAT3, Campbell Scientific Inc., Logan, UT, USA) and an open path infrared gas analyzer (IRGA; model LI-7500, LI-COR Inc., Lincoln, NE, USA), during the 2012 and 2013 growing seasons. The eddy covariance systems were set up at the north end of the plots facing toward the prevailing wind direction, south. The fetch in the south and east-west direction was about 275 m. Sensor heights were adjusted according to the canopy height to avoid measuring fluxes in roughness sub-layer. Other supplementary variables like photosynthetic photon flux density (PPFD – using LI-190, LI-COR Inc., Lincoln, NE, USA), near surface (5 cm depth) soil temperature (using TCAV-L, Campbell Scientific Inc., Logan, UT, USA), soil moisture (using

(CS616, Campbell Scientific Inc., Logan, UT, USA), soil heat flux (G – using HFP01SC, Hukseflux Thermal Sensors B.V., The Netherlands), and above canopy net radiation (R_n – using NR-Lite, Kipp and Zonen, Delft, The Netherlands) were also collected.

We also took periodic biometric measurements for a better understanding of fluxes. Canopy height was recorded and leaf area index (LAI) was measured using a plant canopy analyzer (LAI 2000, LI-COR Inc., Lincoln, NE, USA). Biomass samples were destructively collected from three randomly located 1 m² areas in each field periodically and dried in an oven for a week at 70 °C before recording dry weights.

2.3. Data screening, gap filling, and partitioning of CO₂ fluxes

The eddy flux data, collected at 10 Hz frequency, were processed using the eddy covariance processing software, *EddyPro* (LI-COR Inc., Lincoln, NE, USA). We screened data for the periods of low turbulent intensity ($u^* < 0.20 \text{ m s}^{-1}$) and non-representative footprints (e.g., samples for the period when wind was blowing from behind the tower). Carbon and turbulent fluxes were filtered to keep within the reliable range of fluxes [sensible heat flux, H: -200 to 500 W m⁻² and latent heat flux, LE: -200 to 800 W m⁻² (Sun et al., 2010); and NEE: below -50 μmol m⁻² s⁻¹ (Zeeman et al., 2010). We removed statistical outliers of NEE beyond $\pm 3.5\text{SD}$ (standard deviation) range from a 14-day running mean window. Different gap filling approaches were used based on the length of data gaps. Half-hourly gaps were filled using an average value immediately before and after the gap (Wever et al., 2002). Less than two-hour gaps were filled using linearly interpolated values (Flanagan et al., 2002). Longer data gaps (> 2 hours) were filled using empirical models based on dominant physiological processes. Simple or multiple regression equations or exponential relationships between nighttime NEE (= ER), soil temperature, air temperature, and soil moisture were developed. Finally, the relationships with

the highest level of significance were selected (Flanagan et al., 2002). Mean NEE rates were calculated to fill the gaps for the period when no significant relationships of the variables were found (Flanagan et al., 2002). During daytime, NEE-PPFD or NEE-PPFD-VPD (vapor pressure deficit) relationships were developed to fill large data gaps. Initially, we partitioned daytime NEE into GPP and ER by using a well-established rectangular hyperbolic light-response function (Falge et al., 2001) as shown below:

$$NEE = \frac{\alpha \times GPP_{\max} \times PPFD}{\alpha \times PPFD + GPP_{\max}} + ER \quad (1)$$

where α , i.e. apparent quantum yield, is the initial slope of the light response curve (mol CO₂ mol⁻¹ of photons), PPFD is photosynthetic photon flux density (μmol m⁻² s⁻¹), GPP_{max} is the maximum canopy CO₂ uptake rate (μmol m⁻² s⁻¹) at light saturation, and ER is respiration rate at zero PPFD. Wagle and Kakani (2014c) reported asymmetric diurnal NEE cycles in switchgrass, mainly from June to September, at this site because of the limitation of higher VPD on photosynthesis. Consequently, the equation (1) failed to provide good fits for the NEE data during the period of higher VPD. To address this problem, we calculated GPP_{max} as the exponential decreasing function at high VPD as shown in a previous study (Lasslop et al., 2010):

$$GPP_{\max} = GP_0 \exp(-k(VPD - VPD_0)), \text{ if } VPD > VPD_0 \quad (2)$$

$$GPP_{\max} = GP_0, \text{ if } VPD < VPD_0 \quad (3)$$

where VPD₀ threshold was set to 1 kPa as in Lasslop et al., 2010. Changing this threshold to 2 kPa did not change the results; however, setting the threshold to 3 kPa slightly reduced the coefficient of determination (R²) of the model fits. Model parameters were estimated using nonlinear least squares regression in SAS software (SAS Institute Inc. 2009, Cary, NC, USA). All empirical functions were developed for short time periods (mostly a week and sometimes up to two weeks in the case of insufficient data points or lack of good fits) to account for climatic

variability and seasonality. Only non-gap filled half-hourly data were used to optimize model parameters and to determine the magnitudes and diurnal trends of NEE. Seasonal totals of carbon fluxes were calculated by summing the gap-filled half-hourly flux values. Almost half of the data were gap filled. The sampling uncertainty (gap filling errors) within seasonal sums of carbon fluxes were calculated as the standard error of the gap filling models as described in Black et al. (2007). More details on measurements and data processing techniques have been discussed previously (Wagle and Kakani, 2014b; Wagle and Kakani, 2014c). Sign convention of NEE in this study is: net CO₂ uptake by the ecosystem is negative and net CO₂ release by the ecosystem is positive.

3. Results and discussion

3.1. Weather and crop growth

Because the two flux towers (one in switchgrass and the other in sorghum) were only about 500 m apart, we assumed both species experienced similar weather. Monthly mean maximum temperatures and monthly total rainfalls in 2012 and 2013 in comparison with the 30-year mean for the site are presented in Table 1. As shown, winter and spring 2012 were slightly warmer and wetter compared to the 30-year average, while summer and fall 2012 were slightly warmer and drier. Summer 2013 was relatively cooler and wetter, while the late growing season (August-September) was slightly warmer and drier than the average. Total annual rainfall was 744 and 925 mm in 2012 and 2013, respectively, while the 30-year average (1981 to 2010) annual rainfall for the site was 896 mm.

Because of a warmer and wetter spring in 2012, switchgrass growth initiated earlier in March, about 1.5-2 months earlier than in 2013. Evolution of LAI and dry biomass during the 2012 and 2013 growing seasons is presented in Figure 1. The LAI and biomass were higher in

2012 than they were in 2013. The maximum LAI ($5.9 \text{ m}^2 \text{ m}^{-2}$ for switchgrass and $5.7 \text{ m}^2 \text{ m}^{-2}$ for sorghum) was observed during mid-July 2012 in both ecosystems. In 2013, the maximum LAI was $4.1 \text{ m}^2 \text{ m}^{-2}$ (mid-June) in switchgrass and $5.2 \text{ m}^2 \text{ m}^{-2}$ (end of August) in sorghum. In 2012, the highest recorded aboveground dry biomass in switchgrass was about 1.7 kg m^{-2} (equivalent to 17 t ha^{-1}) during mid-July, while in sorghum it was about 3.0 kg m^{-2} during mid-August. The highest recorded aboveground dry biomass was about 1.3 kg m^{-2} in both ecosystems during 2013. At final harvest, the aboveground dry biomass was 1.19 kg m^{-2} (equivalent to 11.9 t ha^{-1}) in switchgrass (Dec 18th, 2013) and 0.8 kg m^{-2} (equivalent to 8 t ha^{-1}) in sorghum (Jan 20th, 2014). Some foliage loss occurred due to severe freezing and winds at the final harvest. A slight reduction in switchgrass biomass in 2013 compared to 2012 can be attributed to a month delay in green up of switchgrass and water logging conditions in several parts of the fields till mid-June. Consistently higher soil moisture ($> 0.35 \text{ m}^3 \text{ m}^{-3}$, data not shown), from seeding to mid-June, that caused water logging conditions across several parts, and infestation of Johnson grass (*Sorghum halepense* L.) in the sorghum field resulted in substantially lower biomass of sorghum in 2013. The southern part (beyond 100 m from the flux tower) of the sorghum field was infested with Johnson grass in 2013. Glyphosate (@ 2.3 L ha^{-1}) was applied using a wick applicator on 15th and 16th June 2013 and readily suppressed Johnson grass growth.

3.2. Energy balance closure

The plausibility of eddy covariance measurements was assessed from an energy balance closure (EBC) test. We observed the EBC of 0.83 for switchgrass and 0.84 for sorghum for half-hourly measurements for the combined 2012 and 2013 growing seasons (Fig. 2). Our result matches well with the typical range of eddy covariance measurements. The EBC for many field-experiments and for the CO_2 flux networks is about 80% (Aubinet et al., 1999; Wilson et al.,

2002). These results suggest that experimental data could not close the EBC at the Earth's surface. Even a careful application of all corrections of the turbulent fluxes reduced the residual only slightly (Mauder and Foken, 2006). Recently it has been reported that the time-averaged fluxes (Finnigan et al., 2003) or spatially averaged fluxes including turbulent-organized structures (Kanda et al., 2004) can close the energy balance. These findings indicate that the unclosed EBC problem is not related to errors in eddy covariance systems. Instead, it is related to the atmospheric phenomena which eddy covariance systems fail to measure. The EBC adjustment factor was not applied to correct underestimation of CO₂ fluxes in this study.

3.3. Diurnal and seasonal trends of ecosystem CO₂ exchange

Typical diurnal NEE trends in switchgrass and sorghum ecosystems across the growing seasons are compared in Figure 3. Large seasonal and inter-species differences were observed for NEE rates. As expected, higher NEE rates were observed during peak growth due to more canopy photosynthetic capacity and NEE rates declined during the late growing season because of senescence of plants. Similar diurnal NEE patterns were observed in both ecosystems after July. The magnitudes of diurnal peak NEE (monthly average) reached up to -33.02 ± 1.96 (May 2012) and $-36.9 \pm 1.78 \mu\text{mol m}^{-2} \text{s}^{-1}$ (June 2013) in switchgrass, while in sorghum, the values were $-35.9 \pm 2.32 \mu\text{mol m}^{-2} \text{s}^{-1}$ (June 2012) and $-29.6 \pm 1.14 \mu\text{mol m}^{-2} \text{s}^{-1}$ (July 2013). These magnitudes of NEE matched with the results of previous studies in native tallgrass prairie for this region: $-32 \mu\text{mol m}^{-2} \text{s}^{-1}$ in north-central Oklahoma (Suyker and Verma, 2001) and $-30 \mu\text{mol m}^{-2} \text{s}^{-1}$ in northeastern Kansas (Kim and Verma, 1990).

The seasonal courses of daily NEE, GPP, and ER for both ecosystems are shown in Figure 4. A similar seasonal phenology of CO₂ uptake and release were observed over both ecosystems, with maximum carbon uptake during the active growing season followed by a rapid decrease in

the late growing season. High rates of GPP and low rates of ER resulted in substantial rates of carbon uptake by the ecosystems in spring. Drastically different NEE, GPP, and ER patterns can be seen in Figure 4 during July-August between 2012 and 2013 in both ecosystems. As shown, all three components of CO₂ fluxes decreased during July-August 2012 when the site experienced warm and dry weather conditions (Table 1) and increased immediately after rainfall events. Figure 4 shows that carbon fluxes were slightly larger in switchgrass than in sorghum during the late growing season. This is most probably because of deep-rooted switchgrass vegetation could have better access to groundwater since less rainfall was recorded in the late growing season both years. Total rainfall from August to October at this site was 174 mm in 2012 and 139 mm in 2013, while the 30-year average total rainfall during this period was 259 mm (Table 1). Measurement of soil water dynamics during the 2012 and 2013 growing seasons at these study sites showed that soil water content was lower under switchgrass than under sorghum, particularly at deeper depths (Yimam et al., 2014). The maximum rooting depth can exceed 2 m in perennial bioenergy grasses and the maximum root depth of 2.2 m has been used for switchgrass in Soil and Water Assessment Tool (SWAT) and Agricultural Land Management Alternatives with Numerical Assessment Criteria (ALMANAC) models (Kiniry et al., 2005). We did not measure leaf litter on these fields. However, we suspect that more leaf litter accumulation on the soil surface in the switchgrass field might have led to higher microbial respiration rates, resulting in relatively higher ER in the late growing season.

Figure 5 shows steadily increasing (more negative - more carbon uptake by the ecosystem) cumulative NEE from the beginning of the growing season to the end of August and increasing cumulative NEE switched to decreasing NEE after August due to dominance of ER over GPP in both ecosystems. The result shows that the switchgrass ecosystem was a larger carbon sink

throughout the growing season in both years. The seasonal carbon uptake by switchgrass and sorghum was -490 ± 59 and -261 ± 48 g C m⁻² in 2012, and -406 ± 24 and -330 ± 45 g C m⁻² in 2013, respectively (Table 2). More carbon uptake by switchgrass than sorghum, and more carbon uptake by switchgrass in 2012 than in 2013 can be attributed to the differences in carbon uptake period. Monthly average of daily NEE in both ecosystems is presented in Table 3. Switchgrass ecosystem was a net carbon sink from April through August 2012 (5 months), while in 2013 the ecosystem was a sink of carbon from May through August (4 months). Sorghum ecosystem was a net sink of carbon from June through August (3 months) in both years. Higher carbon uptake by sorghum in 2013 compared to 2012 can be attributed to better growing conditions. Drought in the 2012 late growing season caused early yellowing of sorghum plants and reduced the carbon uptake by sorghum (Fig 3, 4).

We are aware that nitrous oxide (N₂O) emissions from these fields can negate carbon gain by these ecosystems as N₂O, a greenhouse gas associated with nitrogen fertilization, is another atmospheric gas of major importance in greenhouse warming. N₂O has approximately 296 times larger global warming potential than that of CO₂ (Solomon et al., 2007). For a full assessment of the greenhouse gas efficiency of these biofuel production systems, N₂O emissions from these fields were not available. A meta-analysis of above-ground N uptake “yield-scaled N₂O emissions” based on 19 independent studies and 147 data points in non-leguminous annual crops showed that N₂O emissions were smallest (about 8.4 g N₂O-N kg⁻¹ N uptake) at N application rate of 180-190 kg ha⁻¹ and then increased rapidly (26.8 g N₂O-N kg⁻¹ N uptake at the application rate of 301 kg N ha⁻¹) after that (Van Groenigen et al., 2010). They also cautioned that N₂O emissions should be assessed as a function of crop N uptake and crop yield instead of fertilizer application rate. Based on their findings, we can expect relatively small yield-scaled N₂O

emissions and more favorable climate impacts from these biofuel production systems with high yield potential, less N demand, and high N use efficiency. In addition, perennial C₄ grasses such as switchgrass translocate significant amount of N from shoots to roots at the end of the growing season (Parrish and Wolf, 1992). It is also important to note that despite detrimental effects of N₂O emissions, N fertilizer application is essential for any crop production to maintain soil nutrient status for the long term.

The cumulative seasonal values of GPP and ER from the switchgrass field were larger than those from the sorghum field (Table 2). The growing season GPP total was $2017 \pm 295 \text{ g C m}^{-2}$ in switchgrass compared to $1164 \pm 183 \text{ g C m}^{-2}$ in sorghum (a ratio of 1.73:1) in 2012. In 2013, cumulative seasonal GPP was 1901 ± 187 and $1356 \pm 173 \text{ g C m}^{-2}$ (a ratio of 1.4:1) in switchgrass and sorghum, respectively. Similarly, the growing season ER total in switchgrass was $1527 \pm 236 \text{ g C m}^{-2}$ compared to $903 \pm 134 \text{ g C m}^{-2}$ in sorghum (a ratio of 1.69:1) in 2012, while it was 1495 ± 163 and $1026 \pm 129 \text{ g C m}^{-2}$ (a ratio of 1.46:1) in switchgrass and sorghum, respectively, in 2013. Because peak daily values of GPP ($19\text{-}20 \text{ g C m}^{-2} \text{ d}^{-1}$) and ER (about $10\text{-}12 \text{ g C m}^{-2} \text{ d}^{-1}$) were similar between ecosystems, the cumulative difference of about 1.7 and 1.4 times higher GPP and ER in switchgrass in 2012 and 2013, respectively, is likely related to the earlier canopy development in switchgrass. Switchgrass greened up in March in 2012 and in April in 2013, while sorghum was planted in May. Both species were killed by frost at the same period (around the first week of November). It shows that switchgrass had one to two months longer growing season compared to sorghum. Our study shows that the growing season ER/GPP ratio was about 0.76-0.78 in both ecosystems. March-August ER/GPP ratio in 2012 and April-August ER/GPP ratio in 2013 was 0.70 in switchgrass. Similarly, May-August ER/GPP ratio was 0.68 in sorghum in both years. During the late growing season (September-October), the

ER/GPP ratio increased in both ecosystems. For switchgrass it was 1.14 in 2012 and 1.32 in 2013; whereas for sorghum, it was 1.42 in 2012 and 1.11 in 2013. The higher ER/GPP ratio after senescence of plants in the late growing season suggests that the carbon balance is linked to plant activity. Growing season ER/GPP ratios of 0.76-0.78 in our study were higher than the previously reported ratios for other ecosystems, most probably due to higher respiration rates and the limitation of photosynthesis in the afternoon hours during warm growing periods in this region as shown in Figure 3. Growing season ER/GPP of 0.56 for maize and 0.76 for soybean (Suyker and Verma, 2012), 0.6 for winter wheat (*Triticum aestivum* L.) and 0.4 for potato (*Solanum tuberosum* L.) and sugarbeets (*Beta vulgaris* L.) (Aubinet et al., 1999) have been reported.

3.4. Magnitudes of ecosystem CO₂ exchange

The magnitude of NEE in switchgrass reached a maximum of -8.53 g C m⁻² d⁻¹ in 2012 and -11.09 g C m⁻² d⁻¹ in 2013, while in sorghum, it was -10.27 and -8.10 g C m⁻² d⁻¹ in 2012 and 2013, respectively. The magnitude of GPP in switchgrass was 18.15 and 20.12 g C m⁻² d⁻¹ in 2012 and 2013, respectively. The maximum rate of GPP in sorghum was 19.03 and 16.28 g C m⁻² d⁻¹ in 2012 and 2013, respectively. Similarly, the peak ER in switchgrass reached 10.66 and 12.39 g C m⁻² d⁻¹ in 2012 and 2013, respectively, while in sorghum, it was 10.24 and 10.01 g C m⁻² d⁻¹ in 2012 and 2013, respectively. The maximal NEE daily value of -11.09 g C m⁻² d⁻¹ (switchgrass) and -10.27 g C m⁻² d⁻¹ (sorghum) in our study was slightly higher than the magnitude of the peak NEE for native tallgrass prairie (-8.4 g C m⁻² d⁻¹) in north-central Oklahoma (Suyker and Verma, 2001). However, these NEE magnitudes were smaller than the magnitude of peak NEE of -17 g C m⁻² d⁻¹ in maize (*Zea mays* L.) in eastern Nebraska (Suyker et al., 2005). Peak GPP values of 19.03 g C m⁻² d⁻¹ (sorghum) and 20.12 g C m⁻² d⁻¹ (switchgrass) in

our study were smaller than those reported for irrigated maize (28-30 g C m⁻² d⁻¹) and rainfed maize (22-27 g C m⁻² d⁻¹) in eastern Nebraska (Suyker and Verma, 2012), but were comparable to values reported for soybean (*Glycine max* L.) (18 g C m⁻² d⁻¹) in Nebraska (Suyker et al., 2005) and a tallgrass prairie (19 g C m⁻² d⁻¹) (Turner et al., 2003). Similarly, peak ER values of about 10-12 g C m⁻² d⁻¹ in switchgrass and sorghum in this study were slightly smaller than those reported by Suyker and Verma (2012) in Nebraska for irrigated maize (12-15 g C m⁻² d⁻¹, but similar with the ER values in rainfed maize (9-13 g C m⁻² d⁻¹). They were also comparable to values reported by Xu and Baldocchi (2004) for grassland in California (9-10 g C m⁻² d⁻¹) and mentioned by Suyker et al. (2005) as unpublished data for a tallgrass prairie (9-9.5 g C m⁻² d⁻¹).

3.5. Response of NEE to VPD and air temperature

We previously demonstrated that VPD of over 3 kPa limited photosynthesis in switchgrass and caused asymmetric diurnal NEE cycles (substantially higher rates of NEE in the morning hours as compared to the afternoon hours at similar light levels) (Wagle and Kakani, 2014a; Wagle and Kakani, 2014c). To compare the effect of VPD on NEE of switchgrass and sorghum, we aggregated half-hourly NEE values in classes of increasing VPD and plotted against VPD (Fig. 6). Results show that NEE of both species increased rapidly with increasing VPD, appeared to approach a maximum value at between 2 and 3 kPa, and decreased thereafter. Scatter plots of NEE against air temperature showed a similar response of NEE to air temperature in both switchgrass and sorghum (Fig. 7a). As shown, NEE increased rapidly with increasing air temperature, appeared to approach a maximum value at slightly over 30 °C, and then reduced markedly beyond 35 °C. The rapid increase of NEE with increasing air temperature and VPD at lower range is because of the fact that air temperature and VPD increase simultaneously, and increasing temperature enhances RuBISCO activity and, in turn, higher carbon assimilation

(Sage and Kubien, 2007). Suppression of carbon fluxes at higher air temperature and VPD is because higher temperatures are also associated with higher VPD which limits carbon assimilation via stomatal closure (Turner et al., 1984) or non-stomatal effect (Morison and Gifford, 1983). More increase in oxygenating reaction of RuBISCO than the carboxylating reaction at high temperatures results in increasing photorespiration and, in turn, reduction in NEE (Long, 1991). Activated RuBISCO is also decreased (Crafts-Brandner and Salvucci, 2000) and heterotrophic respiration is also enhanced at high temperature. To further examine the response of two components (GPP and ER) of NEE to air temperature, we aggregated half-hourly GPP and ER values to increasing air temperature and plotted against air temperature (Fig. 7b, c). Results show that both GPP and ER followed the similar pattern of NEE against air temperature, peaked at slightly over 30 °C and markedly reduced beyond 35 °C. However, GPP reduced greatly than ER at higher temperature, suggesting the temperature sensitivity difference between GPP and ER.

4. Conclusions

Carbon fluxes had similar magnitudes and similar response to air temperature and VPD in both ecosystems. Despite limitation of higher air temperature (>35 °C) and VPD (> 3 kPa) on carbon uptake potential of ecosystems during dry and hot summers in this region, both ecosystems were carbon sinks on seasonal scales. Our results imply that the longer growing season of switchgrass resulted in a relatively larger sink of carbon compared to sorghum. To sum up, our findings provide some guidance on the seasonal carbon dynamics of these two, minimally studied, important biofuel ecosystems and also for predicting the potential impacts of climate change on carbon balances of these biofuels.

400 **Acknowledgements**

401 This research was supported by USDA-NIFA, USDA-DOE Biomass Research and
402 Development Initiative, Grant No. 2009-10006-06070. We thank the field support provided by
403 Jay Prater and Michael Pettijohn. We also thank two anonymous reviewers for their helpful
404 comments on the manuscript. This manuscript is a contribution of the Oklahoma Agricultural
405 Experiment Station, Oklahoma State University, Stillwater, OK.

References

- Aubinet, M. et al., 1999. Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology. Elsevier, pp. 113-175.
- Black, K., Bolger, T., Davis, P., Nieuwenhuis, M., Reidy, B., Saiz, G., Tobin, B., Osborne, B., 2007. Inventory and eddy covariance-based estimates of annual carbon sequestration in a Sitka spruce (*Picea sitchensis* (Bong.) Carr.) forest ecosystem. *Eur. J. For. Res.* 126, 167-178.
- Crafts-Brandner, S.J. and Salvucci, M.E., 2000. Rubisco activase constrains the photosynthetic potential of leaves at high temperature and CO₂. *Proceedings of the National Academy of Sciences*, 97(24): 13430-13435.
- Downing, M. et al., 2011. US billion-ton update: biomass supply for a bioenergy and bioproducts industry, Oak Ridge National Laboratory (ORNL).
- Evers, B.J., Blanco-Canqui, H., Staggenborg, S.A. and Tatarko, J., 2013. Dedicated bioenergy crop impacts on soil wind erodibility and organic carbon in Kansas. *Agronomy Journal*, 105(5): 1271-1276.
- Falge, E. et al., 2001. Gap filling strategies for defensible annual sums of net ecosystem exchange. *Agricultural and Forest Meteorology*, 107(1): 43-69.
- Finnigan, J., Clement, R., Malhi, Y., Leuning, R. and Cleugh, H., 2003. A re-evaluation of long-term flux measurement techniques part I: averaging and coordinate rotation. *Boundary-Layer Meteorology*, 107(1): 1-48.
- Flanagan, L.B., Wever, L.A. and Carlson, P.J., 2002. Seasonal and interannual variation in carbon dioxide exchange and carbon balance in a northern temperate grassland. *Global Change Biology*, 8(7): 599-615.
- Hargreaves, S.K. and Hofmockel, K.S., 2014. Physiological shifts in the microbial community drive changes in enzyme activity in a perennial agroecosystem. *Biogeochemistry*, 117(1): 67-79.
- Kanda, M., Inagaki, A., Letzel, M.O., Raasch, S. and Watanabe, T., 2004. LES study of the energy imbalance problem with eddy covariance fluxes. *Boundary-Layer Meteorology*, 110(3): 381-404.
- Kim, J. and Verma, S.B., 1990. Carbon dioxide exchange in a temperate grassland ecosystem. *Boundary-Layer Meteorology*, 52(1-2): 135-149.
- Kiniry, J. et al., 2005. Switchgrass simulation by the ALMANAC model at diverse sites in the southern US. *Biomass and bioenergy*, 29(6): 419-425.
- Lasslop, G. et al., 2010. Separation of net ecosystem exchange into assimilation and respiration using a light response curve approach: critical issues and global evaluation. *Global Change Biology*, 16(1): 187-208.
- Long, S., 1991. Modification of the response of photosynthetic productivity to rising temperature by atmospheric CO₂ concentrations: has its importance been underestimated? *Plant, Cell & Environment*, 14(8): 729-739.
- Meehan, T.D. et al., 2013. Ecosystem-service tradeoffs associated with switching from annual to perennial energy crops in riparian zones of the US Midwest. *Plos One*, 8(11).
- Mauder, M. and Foken, T., 2006. Impact of post-field data processing on eddy covariance flux estimates and energy balance closure. *Meteorologische Zeitschrift*, 15(6): 597-609.
- Morison, J.I. and Gifford, R.M., 1983. Stomatal sensitivity to carbon dioxide and humidity a comparison of two C₃ and two C₄ grass species. *Plant Physiology*, 71(4): 789-796.

- National Research Council, 2010. Advancing the science of climate change. The National Academies Press, Washington, DC, USA.
- Parrish, D. and Wolf, D., 1992. Managing switchgrass for sustainable biomass production, Proc. Symp. Liquid Fuels from Renewable Resources. Nashville: Nashville Press, pp. 34-39.
- Perlack, R.D. et al., 2005. Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply, DTIC Document.
- Sage, R.F. and Kubien, D.S., 2007. The temperature response of C3 and C4 photosynthesis. *Plant, Cell & Environment*, 30(9): 1086-1106.
- Skinner, R.H. and Adler, P.R., 2010. Carbon dioxide and water fluxes from switchgrass managed for bioenergy production. *Agriculture, ecosystems & environment*, 138(3): 257-264.
- Solomon, S. et al., 2007. IPCC, 2007: climate change 2007: the physical science basis. Contribution of Working Group I to the fourth assessment report of the Intergovernmental Panel on Climate Change.
- Sorrell, S., Speirs, J., Bentley, R., Brandt, A. and Miller, R., 2010. Global oil depletion: A review of the evidence. *Energy Policy*, 38(9): 5290-5295.
- Sun, G. et al., 2010. Energy and water balance of two contrasting loblolly pine plantations on the lower coastal plain of North Carolina, USA. *Forest Ecology and Management*, 259(7): 1299-1310.
- Suyker, A.E. and Verma, S.B., 2001. Year-round observations of the net ecosystem exchange of carbon dioxide in a native tallgrass prairie. *Global Change Biology*, 7(3): 279-289.
- Suyker, A.E. and Verma, S.B., 2012. Gross primary production and ecosystem respiration of irrigated and rainfed maize-soybean cropping systems over 8 years. *Agricultural and Forest Meteorology*, 165: 12-24.
- Suyker, A.E., Verma, S.B., Burba, G.G. and Arkebauer, T.J., 2005. Gross primary production and ecosystem respiration of irrigated maize and irrigated soybean during a growing season. *Agricultural and Forest Meteorology*, 131(3): 180-190.
- Turner, D.P. et al., 2003. A cross-biome comparison of daily light use efficiency for gross primary production. *Global Change Biology*, 9(3): 383-395.
- Turner, N.C., Schulze, E.-D. and Gollan, T., 1984. The responses of stomata and leaf gas exchange to vapour pressure deficits and soil water content. *Oecologia*, 63(3): 338-342.
- FSA, 2013. BCAP: Biomass Crop Assistance Program - Energy Feedstocks from farmers and foresters. A Report by the US Department of Agriculture. Feb 2013. http://fsa.usda.gov/Internet/FSA_File/bcap_documentation.pdf
- USDA, 2010. A USDA regional roadmap to meeting the biofuels goals of the renewable fuels standard by 2022. USDA Biofuels Strategic Production Report, June 23, 2010.
- Van Groenigen, J., Velthof, G., Oenema, O., Van Groenigen, K. and Van Kessel, C., 2010. Towards an agronomic assessment of N2O emissions: a case study for arable crops. *European Journal of Soil Science*, 61(6): 903-913.
- Wagle, P. and Kakani, V.G., 2014a. Environmental control of daytime net ecosystem exchange of carbon dioxide in switchgrass. *Agriculture, Ecosystems & Environment*, 186(0): 170-177.
- Wagle, P. and Kakani, V.G., 2014b. Growing season variability in evapotranspiration, ecosystem water use efficiency, and energy partitioning in switchgrass. *Ecohydrology*, 7(1): 64-72.
- Wagle, P. and Kakani, V.G., 2014c. Seasonal variability in net ecosystem carbon dioxide exchange over a young Switchgrass stand. *GCB Bioenergy*, 6(4): 339-350.

496 Wever, L.A., Flanagan, L.B. and Carlson, P.J., 2002. Seasonal and interannual variation in
 497 evapotranspiration, energy balance and surface conductance in a northern temperate
 498 grassland. *Agricultural and Forest Meteorology*, 112(1): 31-49.

499 Wilson, K. et al., 2002. Energy balance closure at FLUXNET sites. *Agricultural and Forest*
 500 *Meteorology*, 113(1): 223-243.

501 Wofsy, S. and Harriss, R., 2002. The North American Carbon Program (NACP). Report of the
 502 NACP Committee of the US Interagency Carbon Cycle Science Program. US Global
 503 Change Res. Program, Washington, DC.

504 Yimam, Y.T., Ochsner, T.E., Kakani, V.G. and Warren, J.G., 2014. Soil water dynamics and
 505 evapotranspiration under annual and perennial bioenergy crops. *Soil Science Society of*
 506 *America Journal*, 78(5): 1584-1593.

507 Zeeman, M.J. et al., 2010. Management and climate impacts on net CO₂ fluxes and carbon
 508 budgets of three grasslands along an elevational gradient in Switzerland. *Agricultural and*
 509 *Forest Meteorology*, 150(4): 519-530.

510 Zeri, M. et al., 2011. Carbon exchange by establishing biofuel crops in Central Illinois.
 511 *Agriculture, Ecosystems & Environment*, 144(1): 319-329.

Table 1. Monthly mean maximum temperature and monthly total rainfall in 2012 and 2013 in comparison with the 30-year mean (1981-2010) for Chickasha, Oklahoma, USA.

Month	2012		2013		30-year mean	
	Max T (°C)	Rain (mm)	Max T (°C)	Rain (mm)	Max T (°C)	Rain (mm)
Jan	13.56	49.78	11.67	37.85	10.06	33.5
Feb	13	16.26	12.6	73.41	14	45.2
Mar	21.66	112.52	16.65	27.18	18.83	71.9
Apr	24.11	78.74	19.45	268.73	24.06	91.9
May	29.48	150.37	26.48	76.2	28.06	133.1
Jun	33.51	71.37	32.14	112.52	32.39	104.6
Jul	37.98	48.01	33.26	145.03	35.28	53.6
Aug	36.04	42.67	34.3	24.13	34.56	69.3
Sep	31.56	117.35	32.68	48.51	30.61	91.4
Oct	22.61	13.72	23.46	66.55	24.89	98.6
Nov	20.3	21.84	14.56	37.33	17.06	54.4
Dec	12.19	21.84	8.14	7.37	11.5	48.5

Table 2. Growing season sums of net ecosystem CO₂ exchange (NEE), gross primary production (GPP), and ecosystem respiration (ER) ($\pm$ uncertainty) from switchgrass and sorghum fields during their respective growing seasons in 2012 and 2013.

	2012		2013	
	Switchgrass (DOY 61-305)	Sorghum (DOY 122-305)	Switchgrass (DOY 91-304)	Sorghum (DOY 121-304)
GPP (g C m ⁻²)	2017 $\pm$ 295	1164 $\pm$ 183	1901 $\pm$ 187	1356 $\pm$ 173
ER (g C m ⁻²)	1527 $\pm$ 236	903 $\pm$ 134	1495 $\pm$ 163	1026 $\pm$ 129
NEE (g C m ⁻²)	-490 $\pm$ 59	-261 $\pm$ 48	-406 $\pm$ 24	-330 $\pm$ 45

Table 3. Monthly average daily net ecosystem exchange (NEE) of carbon ($\text{g C m}^{-2} \text{ d}^{-1}$) from switchgrass and sorghum fields across the 2012 and 2013 growing seasons. Negative NEE values indicate uptake (i.e., sink) and positive NEE values indicate loss (i.e., source).

	2012		2013	
Months	Switchgrass	Sorghum	Switchgrass	Sorghum
March	0.71			
April	-4.87		1.30	
May	-6.57	0.94	-2.94	1.27
June	-4.82	-7.99	-8.97	-3.8
July	-1.36	-3.25	-3.41	-6.21
August	-0.45	-0.41	-2.0	-2.95
September	0.71	0.81	1.29	0.92
October	0.44	1.21	1.36	0.01

Figure Legends

Fig. 1. Evolution of leaf area index and dry biomass of switchgrass (SWG) and sorghum (SG) during the 2012 and 2013 growing seasons.

Fig. 2. Energy balance closure for the combined 2012 and 2013 growing seasons in switchgrass (a) and sorghum (b).

Fig. 3. Half-hourly binned diurnal courses of net ecosystem CO₂ exchange (NEE) in switchgrass (SWG) and sorghum (SG) across the 2012 (a) and 2013 (b) growing seasons. Each data point is a 30-min time-stamp average value for the entire month. Bars represent standard errors of the means. Negative values of NEE indicate uptake (*i.e.*, sink) and positive values indicate loss (*i.e.*, source) of carbon by the ecosystem.

Fig. 4. Seasonal changes (7-day averages) of net ecosystem CO₂ exchange (NEE), gross primary production (GPP), and ecosystem respiration (ER) in switchgrass (SWG) and sorghum (SG).

Fig. 5. Cumulative weekly net ecosystem CO₂ exchange (NEE) in switchgrass (SWG) and sorghum (SG). Negative value of NEE indicates a net carbon uptake by the ecosystem.

Fig. 6. Response of net ecosystem CO₂ exchange (NEE) to vapor pressure deficit (VPD) in switchgrass (SWG) and sorghum (SG). Half-hourly data for the 2012 and 2013 growing seasons were aggregated in classes of increasing VPD. Bars represent standard errors of the means.

Fig. 7. Response of net ecosystem CO₂ exchange (NEE), gross primary production (GPP), and ecosystem respiration (ER) to air temperature in switchgrass (SWG) and sorghum (SG). Half-hourly data for the 2012 and 2013 growing seasons were aggregated in classes of increasing air temperature. Bars represent standard errors of the means.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7