GCB Bioenergy (2012), doi: 10.1111/j.1757-1707.2012.01189.x

Impacts of herbaceous bioenergy crops on atmospheric volatile organic composition and potential consequences for global climate change

SABER MIRESMAILLI*‡§, MARCELO ZERI*†, ARTHUR R. ZANGERL‡, CARL J. BERNACCHI¶**, MAY R. BERENBAUM*‡ and EVAN H. DeLUCIA*¶

*Energy BioSciences Institute, University of Illinois at Urbana-Champaign, Urbana, IL, USA, †Centro de Ciencia do Sistema Terrestre, Instituto Nacional de Pesquisas Espaciais, Rod. Presidente Dutra, SP-RJ, Cachoeira Paulistra, São Paulo, IL, Brazil, ‡Department of Entomology, University of Illinois at Urbana-Champaign, Urbana, IL, USA, §Sumatics LLC, 575 Madison Ave., New York, NY, USA, ¶Department of Plant Biology, University of Illinois at Urbana-Champaign, Urbana, IL, USA, **Global Change and Photosynthesis Research Unit, Agricultural Research Service, United States Department of Agriculture, Urbana, IL, USA*

Abstract

The introduction of new crops to agroecosystems can change the chemical composition of the atmosphere by altering the amount and type of plant-derived biogenic volatile organic compounds (BVOCs). BVOCs are produced by plants to aid in defense, pollination, and communication. Once released into the atmosphere, they have the ability to influence its chemical and physical properties. In this study, we compared BVOC emissions from three potential bioenergy crops and estimated their theoretical impacts on bioenergy agroecosystems. The crops chosen were miscanthus (*Miscanthus × giganteus*), switchgrass (*Panicum virgatum*), and an assemblage of prairie species (mix of ~28 species). The concentration of BVOCs was different within and above plant canopies. All crops produced higher levels of emissions at the upper canopy level. Miscanthus produced lower amounts of volatiles compared with other grasses. The chemical composition of volatiles differed significantly among plant communities. BVOCs from miscanthus were depleted in terpenoids relative to the other vegetation types. The carbon flux via BVOC emissions, calculated using the flux-gradient method, was significantly higher in the prairie assemblage compared with miscanthus and switchgrass. The BVOC carbon flux was approximately three orders of magnitude lower than the net fluxes of carbon measured over the same fields using eddy covariance systems. Extrapolation of our findings to the landscape scale leads us to suggest that the widespread adoption of bioenergy crops could potentially alter the composition of BVOCs in the atmosphere, thereby influencing its warming potential, the formation of atmospheric particulates, and interactions between plants and arthropods. Our data and projections indicate that, among at least these three potential options for bioenergy production, miscanthus is likely to have lower impacts on atmospheric chemistry and biotic interactions mediated by these volatiles when miscanthus is planted on the landscape scale.

Keywords: atmospheric chemistry, bioenergy, BVOC, global change

Received 21 April 2012 and accepted 16 May 2012

Introduction

Developing renewable energy is a global mandate, and bioenergy is at the center of attention as a viable alternative for fossil fuels. However, widespread planting of bioenergy crops- like all other monoculture-based agricultural systems- can have environmental impacts that should not be overlooked. Most plants release biogenic volatile organic compounds (BVOCs) as signals and cues for pollination (Huber *et al*., 2005; Balao *et al*., 2011), direct and indirect defense (Pare & Tumlinson, 1999; Perera *et al*., 2002; Gershenzon & Dudareva, 2007), and intraspecific communication (Bruce *et al*., 2005; Baldwin *et al*., 2006). Some BVOCs may protect plants against environmental stressors, such as ozone (Loreto & Velikova, 2001) and elevated temperature (Singsaas *et al*., 1997).

In addition to their biological impacts, BVOCs also influence the chemical and physical constituents of the atmosphere (Fall, 2003; Loreto *et al*., 2008; Penuelas & Staudt, 2010). BVOCs are highly reactive with ozone (O_3), hydroxyl radical (OH), and nitrate radical (NO_3) (Loreto *et al*., 2008; Goldstein *et al*., 2009), and can form photochemical oxidants (Finlayson-Pitts & Pitts, 1997) and tropospheric ozone (Chameides *et al*., 1988). BVOCs

Correspondence: Evan H. DeLucia, tel. + 217 333 6177, fax + 217 244 1224, e-mail: deLucia@illinois.edu

in some cases can also contribute to the accumulation of methane and other greenhouse gases (De Carlo *et al.*, 2004). Some chemical reactions in atmosphere can change highly volatile compounds into less volatile compounds (Goldstein & Galbally, 2007), which might consequently form secondary organic aerosol particles with adverse effects on human health (Kavouras *et al.*, 1998; Goldstein *et al.*, 2009).

Different types of BVOCs emitted from plants, in addition to purported bioenergy crops, include: isoprene (Guenther *et al.*, 1995; Carter, 1996; Logan *et al.*, 2000; Monson *et al.*, 2007; Sharkey *et al.*, 2008); green leaf volatiles -oxygenated aldehydes and alcohols- (Heiden *et al.*, 2003; Davison *et al.*, 2008); alcohols (Macdonald & Fall, 1993; Nemecek-Marshall *et al.*, 1995; Atkinson, 2000; Folkers *et al.*, 2008); alkanes and alkenes (Kesselmeier & Staudt, 1999; Atkinson, 2000; Penuelas & Llusia, 2004); and several mono- and sesquiterpenes (Atkinson, 2000; Sakulyanontvittaya *et al.*, 2008). Because the exact composition of BVOC emissions varies with species, the potential impact of different plants, particularly when planted over extensive acreages, on air quality can vary dramatically (Simpson & McPherson, 2011).

The United States Renewable Fuel Standard calls for the production of ~137 billion litres of renewable fuels by 2022 (United States Senate 2007). Currently, corn grain is used to produce ethanol. To meet the targets of the renewable fuel standard with ecologically sustainable crops will involve adding more lignocellulosic crops (second-generation biofuels) to the national energy portfolio (Somerville *et al.*, 2010). Because bioenergy crops are low-density fuels, vast areas of land will be needed, raising the possibility that extensive regions of new crops will change the quantity and composition of BVOCs' emitted to the atmosphere. The objective of this research was to determine the types and amount of different BVOCs emitted to the atmosphere by communities of herbaceous perennial plants that may be suitable as second-generation bioenergy crops planted in the Midwest United States. We compared BVOC chemical composition within and above plant canopy and measured the emission of the BVOCs from three potential bioenergy crops: miscanthus (*Miscanthus* × *iganteus*), switchgrass (*Panicum virgatum*), and a restored prairie assemblage of ~28 species. Despite relatively low rates of biomass production, prairie assemblages have a number of advantages as a bioenergy feedstock, including low requirements for nitrogen and water and high potential for rebuilding biodiversity in agricultural landscapes (Tilman *et al.*, 2006). We predicted that BVOC emissions would be greater from the mixed prairie given than either miscanthus or switchgrass given its greater species diversity. For the same reason, we also predicted greater complexity in the BVOCs from the prairie assemblage.

Methods

Description of field site

Measurements were conducted at the University of Illinois 'Energy Farm' located in Urbana, IL, USA (40°3′ 46.209″N, 88° 11′ 46.0212″W, ~220 m above sea level). Plots (4 ha) of miscanthus (*Miscanthus* × *giganteus*), switchgrass (*Panicum virgatum*), and restored prairie (mix of ~28 species) were established in 2008. Because of poor establishment, the miscanthus plot was replanted in 2010. The prairie, described in Zeri *et al.* (2011), was composed of 28 species representing the major functional groups typical of this community type. Atmospheric samples were collected at the center of each 4 ha plot.

The soil is a Flanagan-Drummer soil series (fine-silty, mixed, mesic Typic Endoaquoll, typical of northern and central Illinois). The field is tile-drained and, prior to establishing the energy crops, was in continuous cultivation of arable crops. According to the Illinois State Water Survey, at this location the mean temperature was 11.1 °C and the mean accumulated rainfall was 1041.7 mm (averaged from 1979 to 2009, http://www.isws.illinois.edu/data.asp). The volatile collection towers were installed next to eddy covariance towers at the center of each plot. More information about the eddy covariance instrumentation and results can be found in Zeri *et al.* (2011).

Volatile collection from the atmosphere

Biogenic volatile organic compounds were collected from the atmosphere near each vegetation type between June and August 2010, near the time of maximum aboveground biomass (July–August; K. Anderson-Teixeira, unpublished results). We used adsorption/desorption technique, commonly used by chemical ecologists (D'Alessandro & Turlings, 2006). This method provides adequate sensitivity for certain volatile measurements and enables a great number of compounds to be monitored. We used this volatile collection technique in conjunction with gradient flux measurement method to estimate the flux of BVOCs between vegetation and the atmosphere (Hewitt *et al.*, 2011). The gradient flux method requires that eddy diffusivity be known for the time periods in which the measurements were made. These measures of eddy diffusivity were collected using a three-dimensional sonic anemometer (Model 81000VRE; R.M. Young Company, Inc., Traverse City, MI, USA) that is integrated into an eddy covariance system located in the center of each plot. In addition to providing measure of eddy diffusivity, the eddy covariance measurements of carbon dioxide, sensible heat and latent heat fluxes provide an opportunity to pair the fluxes of BVOCs with other key biological fluxes (Greenberg *et al.*, 2003; Zeri *et al.*, 2011).

Proton Transfer Reaction-Mass Spectrometry (PRT-MS) is an instrument that has been widely utilized in atmospheric BVOC analysis. Although PRT-MSs are highly sensitive and

viable field instruments for trace analysis of certain compounds (Karl *et al*., 2005; Graus *et al*., 2010; Mielke *et al*., 2010; Schaub *et al*., 2010), analysis with GC-MS still is necessary for definitive identification of compounds (De Gouw *et al*., 2003). We are not aware of any direct comparison of GC-MS and PRT-MS for evaluation of their analytical capabilities. GC-MS has been extensively used over the past 30 years by chemical ecologists for similar analyses at a substantially lower cost compare with PRT-MS (Millar & Haynes, 1998). The lower cost of the adsorption/desorption technique makes it possible to collect multiple samples at different locations. A major limitation of our method, however, was lack of sensitivity to isoprene. This simple terpene makes up the large percentage of global BVOC emissions from certain plants species, notably poplars, but is not likely to be emitted from grasses (Harley *et al*., 1999; Lerdau & Gray, 2003; Yuan *et al*., 2009).

To measure the distribution of BVOCs within the plant canopy, sampling towers were erected in each vegetation type; the canopies then were divided into four 50 cm sections (starting 20 cm below the highest part of plant canopy toward the ground) and volatiles were collected from each section (Fig. 1). Collections within plant canopies were repeated at four different randomly selected locations in each vegetation type (at 2 weeks intervals between collections).

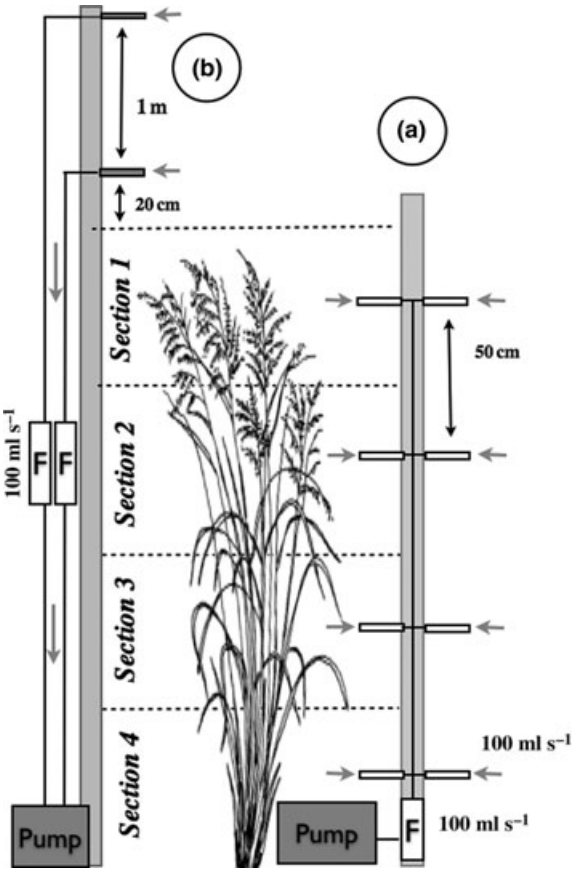

Fig. 1 Volatile collection and extraction methods: (a) volatile collection tower within plant canopy and (b) volatile collection tower above plant canopy.

An additional set of measurements was made at two heights above the canopy of each vegetation type (20 cm and 120 cm, Fig.1c) to calculate atmospheric exchange of BVOCs using the flux-gradient method (see vertical fluxes of BVOCs for more details). Above-canopy collections were repeated four times for switchgrass and restored prairie, and five times for miscanthus.

At each sampling height, BVOCs were collected by drawing air through tubes containing two different types of adsorbent materials. Porapak™ type Q (80/100 mesh; Waters Corporation, Milford, MA, USA- 300 mg Porapak inside 10 cm long, 0.5 cm ID Teflon tube secured with metal mesh) was used for collections within plant canopies, and TENAX™ type GR (60/80 mesh; Scientific Instrument Services Inc., Ringoes, NJ, USA- 1 g TENAX inside 10 cm long, 0.5 cm ID stainless steel tubes secured with metal mesh) was used in collections above plant canopies. TENAX GR has a higher breakthrough volume (the volume at which a particular solute pumped continuously through a column begins to elute) for most volatiles and lower affinity for water, which makes it a suitable choice for collection of volatiles from the air above the plant canopy in windy conditions. Tenax and Porapak provide qualitatively similar results; nevertheless, direct quantitative comparisons of results derived from these different adsorbent materials were avoided.

All air sample collections were conducted for 1 h with the following airflows: 25 mL min^{-1} per tube in volatile chambers (total of 4 tube, 6 L of air per chamber), 12.5 mL min^{-1} per tube in qualitative trials within the plant canopy (total of 8 tubes, 1.5 L of air per canopy section), and 100 mL min^{-1} per tube in quantitative trials above the plant canopy (total of two tubes, 6 L of air at each height). The airflow was adjusted with a precision flow meter (Single tube flow meter model P; AALBORG Instruments & Controls Inc., Orangeburg, NY, USA). A battery-operated vacuum pump (AirCheck® XR5000; SKC Inc., PA, USA) was used in all trials.

Volatile extraction and analysis

We used solvent and thermal desorption to extract volatiles from the adsorbents. With Porapak tubes, volatiles were extracted with 1 mL of hexane (98.5%; Sigma-Aldrich, St. Louis, MO, USA) into a 3 mL GC vial. For the TENAX tubes, we extracted the volatiles using a thermal extraction system consist of a heating block maintained at 60 °C with an insert for the TENAX tube connected to a Luer lock GC needle (Gauge 26, metal hub, 12.5 cm length; Hamilton, Reno, NV, USA) that guided the volatiles to a 3 mL GC vial with an insert filled with 200 μL of hexane. The volatiles were gently pushed out of the tubes with nitrogen (5 kPa for 1 min) while heated at 60 °C (Fig. 1d). The volatiles in each sample were then analyzed by gas chromatograph-mass spectrometer (GC-MS). The GC-MS (QP2010nc-Plus; Shimadzu, Baltimore, MD, USA) was fitted with a SHRx1-5MS (DB-5) column (30 m × 0.25 mm ID, 0.25 mm DF), and samples were run using the following temperature program: 40 °C for 2 min, 8 °C min^{-1} to 250 °C hold for 5 min. Tridecane (Aldrich 99 + %) was used as internal standard.

System calibration

Commercially available authentic standards were used for calibration of GC-MS. Serial dilutions of standards were analyzed with the machine and calibration curves were developed. To test recovery rate of adsorption tubes, known amount of standard materials were placed inside 40 mL vials sealed with silicon septa and allowed to volatilize overnight at room temperature. The compounds then were collected from the vials and trapped on the Porapak or TENAX tubes via a Luer lock needle inserted in the vial through the septum. Compounds were extracted from the tubes and recovery rates and correction factors were calculated as in Miresmailli *et al.* (2010a,b).

Vertical fluxes of BVOCs

The fluxes of BVOCs (F_{BVOC}) between vegetation and the atmosphere were calculated using the flux-gradient method (Pasquill, 1950; Businger *et al.*, 1971; Arya, 2001; Pattey *et al.*, 2006), which requires the knowledge of vertical gradients of BVOCs above the canopy and other auxiliary measurements. The vertical flux of BVOCs was calculated as follows:

$$F_{BVOC} = \frac{-u_* k(\rho_2 - \rho_1)}{\left[\ln\left(\frac{z_2 - d}{z_1 - d}\right) - \Psi_{z_2} + \Psi_{z_1}\right]};$$

where u_* is the friction velocity, k is the Von Kármán constant (0.4), ρ_1 and ρ_2 are the BVOCs concentrations at heights z_1 and z_2 above the canopy, respectively, d is the displacement height (~2/3 of the canopy height), and Ψ_{z_1} and Ψ_{z_2} are the integrated similarity functions for heat at heights z_1 and z_2 (Hicks, 1976; Stull, 1988). The similarity functions require knowledge of the Monin-Obukhov length L, which in turn requires the latent and sensible heat fluxes and the friction velocity u_*. Those variables were obtained from the eddy covariance measurements that corresponded to the same times that the BVOC samples were collected. Auxiliary measurements included air temperature, relative humidity, solar radiation components, and other meteorological variables. Details about the eddy covariance system and meteorological instrumentation at each plot were described elsewhere (Zeri *et al.*, 2011). The eddy covariance method has been previously used for VOC measurement (Guenther *et al.*, 2001; Warneke *et al.*, 2002).

Statistics

Univariate and multivariate GLM were used to analyze the volatile data (SPSS Ver. 18 Software; IBM Corporation, Somers, NY, USA) as a function of vegetation type and height within the canopy. Plots within each vegetation type were treated as independent replicates; however, because vegetation type was not replicated, the statistical analysis does not distinguish between 'plot' and 'vegetation type.' Because the four plots were established next to one another on agricultural land of uniform slope and soil type, we interpreted our results to mean that differences among plots derived from differences in vegetation type.

Results

The concentrations of BVOCs declined with canopy depth and were significantly different among vegetation types. The main effects of canopy section ($F_{3,48} = 14.998$, $P < 0.05$) and crop type ($F_{2,48} = 7.503$, $P < 0.05$) on BVOC concentrations were significant, yet no significant interaction was found between crop type and canopy section ($F_{6,48} = 1.932$, $P = 0.10$). The BVOC concentration within the miscanthus canopy was lower than in other crops (Fig. 2a).

Volatiles were sorted into distinct chemical groups (e.g. green leaf volatiles, alcohols, alkanes, alkenes, terpenoids, and other VOCs) based on their biological importance and their impact on atmospheric chemistry. Although there was no main effect of vegetation type ($F_{2,288} = 0.030$, $P = 0.97$) or canopy height ($F_{3,288} = 0.033$, $P = 0.99$) on the composition of BVOCs, significant two-way interactions [vegetation type × chemical groups ($F_{10,288} = 23.965$, $P < 0.05$) and canopy height × chemical groups ($F_{15,288} = 3.118$, $P < 0.05$)] indicated that the composition of BOVCs (qualitative percentage) within plant canopies was different among crops. Although volatile blends of all plants consisted of all aforementioned chemical groups (with the exception of BVOCs from miscanthus, which were depleted in terpenoids relative to the other vegetation types, Fig. 2b), the presence of individual compounds within each group differed among vegetation types. For example, hexenal, a widespread green leaf volatile, was absent from the miscanthus volatile blend. In contrast, *Z*-3-hexenyl acetate (another GLV) was found in all three crops (Table 1).

The flux of carbon in BVOCs was significantly higher from prairie than miscanthus or switchgrass ($F_{2,26} = 8.035$, $P < 0.05$) (Fig. 3a), but was a small fraction of total carbon exchange with the atmosphere for all vegetation types (Fig. 3b). Environmental factors, such as air temperature ($P = 0.57$), vapor pressure deficit ($P = 0.67$), solar radiation ($P = 0.23$), and wind velocity ($P = 0.23$), were not correlated with the BVOC fluxes. Whereas rates of isoprene emissions are coupled to the rate of photosynthesis and vary with light and temperature (Lerdau & Gray, 2003), monoterpene emission occurs from a leaf reservoir and is uncoupled from instantaneous controls over biosynthesis (Monson *et al.*, 1995). Miscanthus was a stronger carbon sink than either switchgrass or prairie, as indicated by its larger net ecosystem exchange of CO_2 ($F_{2,12} = 30.732$, $P < 0.05$) (Fig. 3b). The proportion of carbon losses as BVOCs relative to carbon uptake was less for miscanthus than for the other vegetation types. The composition of BVOCs above the plant canopies also varied; the composition of volatiles above the miscanthus canopy was depleted in

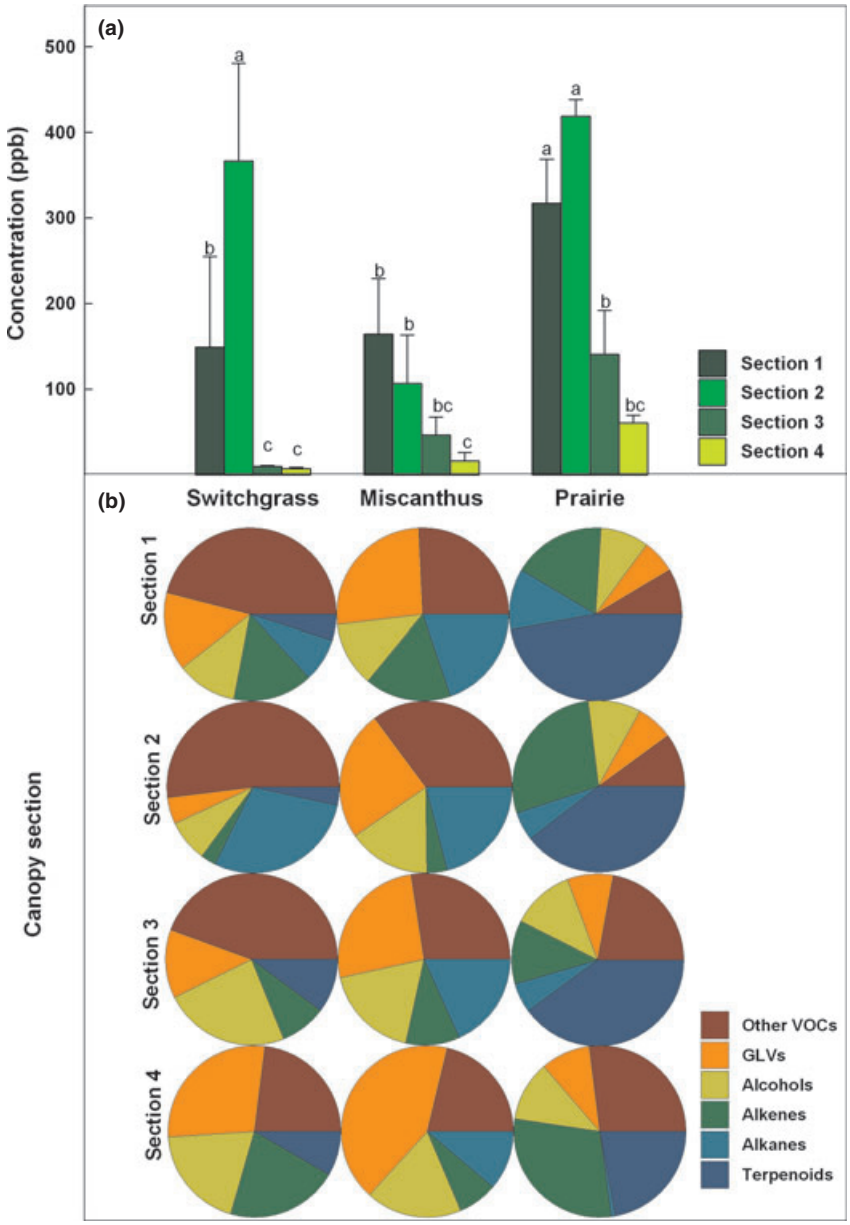

Fig. 2 Panel A: BVOCs concentration (ppb) within plant canopy at different heights (section one starts at 20 cm below the highest part of plant canopy with 50 cm between each section). Bars representing the mean concentration of BVOCs within 1.5 L of air sampled from each canopy section (+SE) obtained through 1 h continuous collection at a rate of 12.5 mL min^{-1}, letters on the bars indicate significant differences of the means (separated using Tukey's test); Panel B: Percentage of different chemical groups (green leaf volatiles, alcohols, alkenes, alkanes, terpenoids, and other volatiles-see Table 1) at different sections of plant canopy.

terpenoids and green leaf volatiles relative to the other vegetation types (Fig. 3c).

The concentration of BVOCs at closer proximity (20 cm) above the plant canopy was significantly different among the plants ($F_{2,13} = 9.230$, $P < 0.05$) with prairie producing twice the levels of BVOCs as miscanthus and switchgrass. However, no significant differences were found in the BVOC concentration at the greater height (120 cm) above the canopy ($F_{2,13} = 0.048$, $P = 0.850$).

The composition (qualitative percentage) of BVOCs also was significantly different above the plant canopies ($F_{5,156} = 77.691$, $P < 0.05$). Miscanthus volatiles contained no terpenoids and had significantly lower amounts of green leaf volatiles compared with the other plants. There was a significant interaction between crop,

Table 1 Major volatile compounds emitted from miscanthus (MXG), switchgrass (SW) and prairie plants (PRG)

Plant based BVOCs	MXG	SW	PRG	Class
Methanol	✓	✓	✓	Alcohols
Penten-3-ol		✓		
2-Octen-1-ol		✓		
Butan-2-ol			✓	
Dodecane	✓		✓	Alkanes
Tetradecane		✓	✓	
Ethylbenzene			✓	Alkenes
Benzene 1,2 diethyl	✓		✓	
Z-2-Butene	✓			
2-Methyl-1-butene	✓			
3-Methyl-1-butene		✓		
Hexanal		✓	✓	GLVs
Hexan-3-ol		✓	✓	
Z-3-Hexenyl acetate	✓	✓	✓	
Z-3-Hexenal	✓	✓		
Camphene			✓	Terpenoids
β-Phellandrene			✓	
β-Pinene			✓	
β-Myrcene		✓	✓	
d-Limonene			✓	
3-Carene		✓	✓	
α-Pinene			✓	
Acetaldehyde	✓	✓		Other VOCs
Benzaldehyde	✓		✓	
Butanoic acid ethyl ester	✓	✓	✓	

volatile groups, and distance above the canopy ($F_{5,156} = 4.136$, $P < 0.05$). In view of the differences in individual compounds of each volatile group among crops, our results indicate that the miscanthus BVOC blend is not as persistent as that of switchgrass and restored prairie in close proximity to the plant canopy.

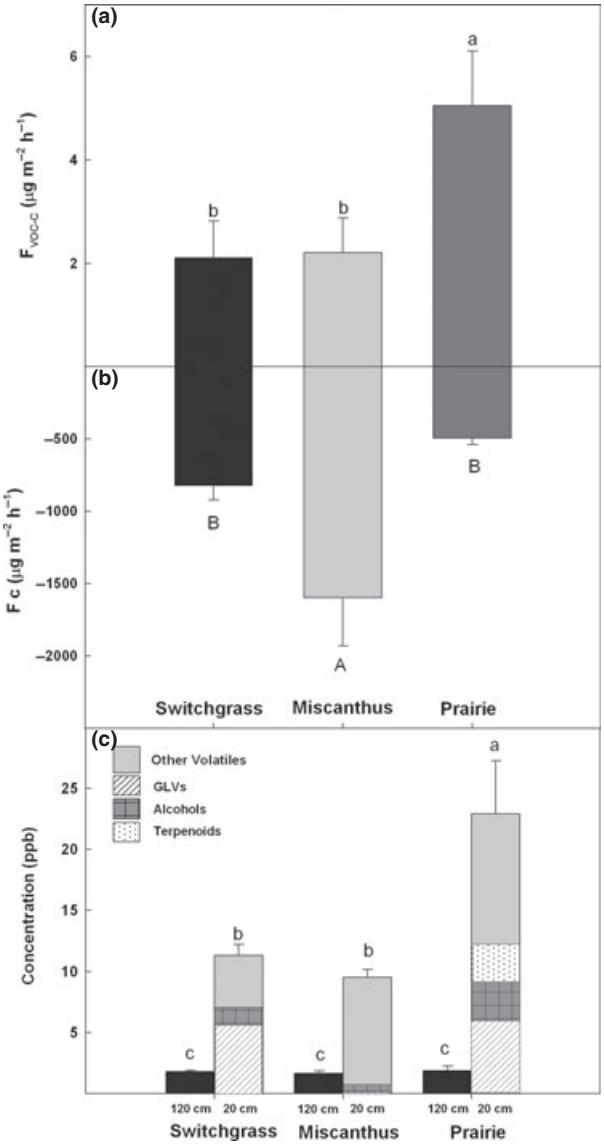

Fig. 3 Panel A: Flux of carbon via emission of BVOCs. Bars representing mean (+SE); Panel B: Flux of carbon obtained from CO_2 eddy covariance. Bars representing mean (+SE), letters on the bars indicate significant differences of the means (separated using Tukey's test); and Panel C: BVOCs concentration and composition above plant canopy at two different heights (20 cm and 120 cm). Bars representing the mean concentration of BVOCs within 6 L of air sampled at each height (+SE) obtained through 1 h continuous collection at a rate of 100 mL min^{-1}, letters on the bars indicate significant differences of the means (separated using Tukey's test); Concentrations of green leaf volatiles, alcohols, and terpenoids at 20 cm above plant canopies were marked with stack bars. No significant differences were found in the BVOC concentration and composition in volatile samples captured at 120 cm above the canopy (marked by black bars).

Discussion

The widespread adoption of bioenergy crops can potentially alter the composition of BVOCs in the atmosphere, thereby influencing its warming potential, the formation of atmospheric particulates, and interactions between plants and arthropods. Almost all of the chemicals we isolated from the volatile blends of the crops under study have been reported previously from other plant species (Fedele *et al*., 2007; Eller *et al*., 2011) (Table 1; Table S1); however, the composition of these blends varied among different plant canopies. The prairie assemblage consisted of several species (dicots and monocots), many of which were flowering at the time of sampling, and hence produced a volatile blend with greater numbers and higher concentrations of volatile compounds. In contrast, switchgrass and miscanthus are single species, so the difference in their volatile composition might be due to species-specific differences between these two plants (Lerdau & Gray, 2003; Simpson & McPherson, 2011).

Differences in the production of volatiles among bioenergy feedstock crops have the potential to alter biotic interactions on the landscape scale. Insects use both visual and chemical stimuli for finding hosts (Bernays & Champan, 1994). When a flying insect approaches a new host plant, it generally first follows visual cues and in closer proximity to the plant canopy uses chemical cues to find potential host plant. Both switchgrass and native prairie had higher concentration of volatiles on the uppers parts of the canopy compared with miscanthus and thus may be more susceptible to discovery by host-seeking herbivores. BVOC composition can also change the behavior of arthropods that utilize the volatile chemical cues as a source of information and thus possibly alter biomass losses to herbivores (Isman & Miresmailli, 2011). BVOC composition also can influence plant-pathogen interactions (Eastburn *et al*., 2011; Pangga *et al*., 2011) and thus the likelihood and severity of crop disease epidemics (Fitt *et al*., 2011).

Biogenic volatile organic compounds have direct impacts on atmosphere warming potential because they are precursors of particulate matter (Loreto *et al*., 2008; Penuelas & Staudt, 2010). BVOCs are highly reactive and, in the presence of ozone, hydroxyl, and nitrate radicals, can form photochemical oxidants (Finlayson-Pitts & Pitts, 1997). BVOCs are important precursors to the formation of tropospheric ozone (Chameides *et al*., 1988), contribute to the accumulation of methane and other greenhouse gases (De Carlo *et al*., 2004), and consequently form secondary organic aerosol particles with adverse effects on human health (Kavouras *et al*., 1998). Terpenoids are among the major BVOCs that can alter atmospheric chemistry (Guenther *et al*., 1995; Carter, 1996). We found that miscanthus BVOCs were depleted in terpenoids relative to the other vegetation types (Fig. 2b; 3c). Green leaf volatiles (oxygenated aldehydes and alcohols) are another group of BVOCs with atmospheric importance (Heiden *et al*., 2003; Davison *et al*., 2008). We observed a significant decrease in GLVs level above the miscanthus canopy. Miscanthus volatiles lack some prominent GLVs that were found in both switchgrass and prairie (Table 1), so the lower percentage of the GLV group in miscanthus might be due to differences in its BVOC composition.

Biogenic volatile organic compounds emissions are temporally dynamic (Pio *et al*., 2005), changing with environmental conditions (Owen *et al*., 2002; Tarvainen *et al*., 2005) and plant development (Shiojiri & Karban, 2006). Several studies reported a significant increase in BVOC emission from senescing crops (Karl *et al*., 2005) and during harvest (Guenther *et al*., 2001; Lindinger *et al*., 2001; Warneke *et al*., 2002; Kirstine & Galbally, 2004). Our focus in this experiment, however, was on the emission of BVOCs during the growing season when crops are susceptible to herbivores that might use these volatiles as host finding cues. On the basis of our findings, we project that miscanthus BVOCs will be at lowest risk of arthropod discovery based on olfaction-mediated host location during the growing season, and perhaps as well lower overall atmosphere warming potential and particle formation compared with switchgrass and native prairie.

The emission of BVOCs represents a loss of carbon from ecosystems that can at times be a significant fraction of net primary production. While losses of isoprene typically are less than 3% of net primary production, in some oak forests these losses can amount to ~12% (Kesselmeier *et al*., 2002). The emission of monoterpenes, however, is expected to be much smaller percentage of net primary production than isoprene (Kuhn *et al*., 2007). We calculated the hypothetical maximum flux of BVOC emissions by extrapolating to the whole year the average fluxes obtained when the crops were fully developed (June–August). We assumed that BOVC emissions were constant through time and were not influenced by variation in environmental factors, producing an estimate of the theoretical maximum annual flux of BVOCs. Despite their biological and atmospheric importance, the data presented here suggest that nonmethane/nonisoprene BVOCs emitted from these bioenergy grasses will not play a significantly important role in the ecosystem carbon budget.

The theoretical maximum annual carbon flux via BVOC emissions in these potential bioenergy crops was considerably lower than BVOC fluxes from other vegetation (Sakulyanontvittaya *et al*., 2008). The estimated annual carbon losses through BVOC emission for our crops were as follows: ~195 g ha^{-1}, for miscanthus; ~185 g ha^{-1}, for switchgrass; and ~443 g ha^{-1}, for prairie. In a recent review, Sakulyanontvittaya *et al.* (2008) used field measurements and literature values to estimate mono- and sesquiterpene fluxes emitted from different vegetation types including some grasses and crops (fennel, tomato, sunflower, corn, bean, wheat, and tobacco) in the United States (Sakulyanontvittaya *et al*., 2008). Using the estimates of Sakulyanontvittaya *et al.* (2008) and applying our assumptions, we calculated the annual amount of α- pinene – one of the most important monoterpenes with adverse effects on atmospheric chemistry – emitted from those species to be ~5010 g ha^{-1} (volatiles were collected within closed chambers). Despite methodological differences, in general, our bioenergy grass species emit lower amounts of BVOCs when compared with corn, soybean, and other grass species. A side-by-side analysis of BVOC emissions from different crops is necessary to make a definitive comparison. Our data and projections, however, allow us to state that, among at least these three potential

options for bioenergy production, miscanthus is likely to have lower impacts on atmospheric chemistry and biotic interactions mediated by these volatiles when planted on the landscape scale.

Acknowledgment

The Energy Biosciences Institute funded this research. The authors thank Alan Yanahan, Allen Lawrance, Robert Orpet, Jacob Becraft, and Olivia Niziolek for their assistance with data collection.

References

Arya SP (2001) *Introduction to Micrometeorology*. Academic Press, San Diego.

Atkinson R (2000) Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment*, **34**, 2063–2101.

Balao F, Herrera J, Talavera S, Dotterl S (2011) Spatial and temporal patterns of floral scent emission in *Dianthus inoxianus* and electroantennographic responses of its hawkmoth pollinator. *Phytochemistry*, **72**, 601–609.

Baldwin IT, Halitschke R, Paschold A, Von Dahl CC, Preston CA (2006) Volatile signaling in plant-plant interactions: "talking trees" in the genomics era. *Science*, **311**, 812–815.

Bernays EA, Champan RF (1994) *Host-Plant Selection by Phytophagous Insects*. Chapman & Hall, New York, USA.

Bruce TJ, Wadhams LJ, Woodcock CM (2005) Insect host location: a volatile situation. *Trends in Plant Science*, **10**, 269–274.

Businger JA, Wyngaard JC, Izumi Y, Bradley EF (1971) Flux-profile relationships in atmospheric surface layer. *Journal of the Atmospheric Sciences*, **28**, 181–189.

Carter WP (1996) Condensed atmospheric photooxidation mechanisms for isoprene. *Atmospheric Environment*, **30**, 4275–4290.

Chameides WL, Lindsay RW, Richardson J, Kiang CS (1988) The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science*, **241**, 1473–1475.

D'Alessandro M, Turlings TC (2006) Advances and challenges in the identification of volatiles that mediate interactions among plants and arthropods. *The Analyst*, **131**, 24–32.

Davison B, Brunner A, Ammann C, Spirig C, Jocher M, Neftel A (2008) Cut-induced VOC emissions from agricultural grasslands. *Plant Biology (Stuttgart, Germany)*, **10**, 76–85.

De Carlo P, Brune WH, Martinez M *et al.* (2004) Missing OH reactivity in a forest: evidence for unknown reactive biogenic VOCs. *Science*, **304**, 722–725.

De Gouw J, Warneke C, Karl T, Eerdekens G, Van Der Veen C, Fall R (2003) Sensetivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry. *International Journal of Mass Spectrometry*, **224**, 365–382.

Eastburn DM, Mcelrone AJ, Bilgin DD (2011) Influence of atmospheric and climate change on plant-pathogen interactions. *Plant Pathology*, **60**, 54–69.

Eller ASD, Sekimoto K, Gilman JB *et al.* (2011) Volatile organic compound emissions from switchgrass cultivars used as biofuel crops. *Atmospheric Environment*, **45**, 3333–3337.

Fall R (2003) Abundant oxygenates in the atmosphere: a biochemical perspective. *Chemical Reviews*, **103**, 4941–4952.

Fedele R, Calbally IE, Porter N, Weeks IA (2007) Biogenic VOC emissions from fresh leaf mulch and wood chips of *Grevillea robusta* (Australian Silky Oak). *Atmospheric Environment*, **41**, 8736–8746.

Finlayson-Pitts BJ, Pitts JN Jr (1997) Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles. *Science*, **276**, 1045–1052.

Fitt BDL, Fraaije BA, Chandramohan P, Shaw MW (2011) Impact of changing air composition on severity of arable crop disease epidemics. *Plant Pathology*, **60**, 44–53.

Folkers A, Huve K, Ammann C *et al.* (2008) Methanol emissions from deciduous tree species: dependence on temperature and light intensity. *Plant Biology (Stuttgart, Germany)*, **10**, 65–75.

Gershenzon J, Dudareva N (2007) The function of terpene natural products in the natural world. *Nature Chemical Biology*, **3**, 408–414.

Goldstein AH, Galbally IE (2007) Known and unknown organic constituents in the earth' s atmosphere. *Environmental Science and Technology*, **41**, 1514–1521.

Goldstein AH, Koven CD, Heald CL, Fung IY (2009) Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States. *Proceedings of the National Academy of Sciences, USA*, **106**, 8835–8840.

Graus M, Muller M, Hansel A (2010) High resolution PTR-TOF: quantification and formula confirmation of VOC in real time. *Journal of the American Society of Mass Spectrometry*, **21**, 1037–1044.

Greenberg JP, Guenther A, Harley P *et al.* (2003) Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana. *Journal of Geophysical Research D Atmospheres*, **108**, 8466–8476.

Guenther A, Hewitt CN, Erickson D *et al.* (1995) A global-model of natural volatile organic-compound emissions. *Journal of Geophysical Research D Atmospheres*, **100**, 8873–8892.

Guenther A, Karl T, Lindinger C, Jordan A, Fall R, Lindinger W (2001) Eddy covariance measurements of oxygenated volatile organic compound fluxes from crop harvesting using a redesigned proton-transfer-reaction mass spectrometer. *Journal of Geophysical Research D Atmospheres*, **106**, 24157–24167.

Harley PC, Monson RK, Lerdau MT (1999) Ecological and evolutionary aspects of isoprene emission from plants. *Oecologia*, **118**, 109–123.

Heiden A, Kobel K, Langebartels C, Schuth-Thomas G, Wildt J (2003) Emission of oxygenated volatile organic compounds from plants part I: emission from lipoxygenase activity. *Journal of Atmospheric Chemistry*, **45**, 143–172.

Hewitt CN, Langford B, Possell M, Karl T, Owen SM (2011) Quantification of VOC emission rates from the biosphere. *Trends in Analytical Chemistry*, **30**, 937–944.

Hicks BB (1976) Wind profile relationships from Wangara experiment. *Quarterly Journal of the Royal Meteorological Society*, **102**, 535–551.

Huber FK, Kaiser R, Sauter W, Schiestl FP (2005) Floral scent emission and pollinator attraction in two species of *Gymnadenia* (Orchidaceae). *Oecologia*, **142**, 564–575.

Isman MB, Miresmailli S (2011) Plant Essential Oils as Repellents and Deterrents to Agricultural Pests. In: *Recent developments in invertebrate repellents* (ed. Paluch G), pp. 67–77. American Chemical Society. Washington, DC.

Karl T, Harren F, Warneke C, De Gouw JA, Grayless C, Fall R (2005) Senescing grass crops as regional sources of reactive volatile organic compounds. *Journal of Geophysical Research D Atmospheres*, **110**, D15302.

Kavouras IG, Mihalopoulos N, Stephanou EG (1998) Formation of atmospheric particles from organic acid produced by forests. *Nature*, **395**, 683–686.

Kesselmeier J, Staudt M (1999) Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. *Journal of Atmospheric Chemistry*, **33**, 23–88.

Kesselmeier J, Ciccioli P, Kuhn U *et al.* (2002) Volatile organic compound emissions in relationto plant carbon fixation and the terrestrial carbon budget. *Global Biogeochemical Cycles*, **16**, 73–82.

Kirstine WV, Galbally IE (2004) A simple model for estimating emissions of volatile organic compounds from grass and cut grass in urban airsheds and its application to two Australian cities. *Journal of the Air & Waste Management Association*, **54**, 1299–1311.

Kuhn U, Andreae MO, Ammann C *et al.* (2007) Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurments, and implication on the atmospheric chemistry and local carbon budget. *Atmospheric Chemistry and Physics*, **7**, 2855–2879.

Lerdau M, Gray D (2003) Ecology and evolution of light-dependent and light-indpendent pytogenic volatile organic carbon. *New Phytologist*, **157**, 199–211.

Lindinger W, Karl T, Guenther A, Jordan A, Fall R (2001) Eddy covariance measurement of biogenic oxygenated VOC emissions from hay harvesting. *Atmospheric Environment*, **35**, 491–495.

Logan BA, Monson RK, Potosnak MJ (2000) Biochemistry and physiology of foliar isoprene production. *Trends in Plant Science*, **5**, 477–481.

Loreto F, Velikova V (2001) Isoprene produced by leaves protects the photosynthetic apparatus against ozone damage, quenches ozone products, and reduces lipid peroxidation of cellular membranes. *Plant Physiology*, **127**, 1781–1787.

Loreto F, Kesselmeier J, Schnitzler JP (2008) Volatile organic compounds in the biosphere-atmosphere system: a preface. *Plant Biology (Stuttgart, Germany)*, **10**, 2–7.

Macdonald RC, Fall R (1993) Detection of substantial emissions of methanol from plants to the atmosphere. *Atmospheric Environment*, **27**, 1709–1713.

Mielke LH, Pratt KA, Shepson PB, Mcluckey SA, Wisthaler A, Hansel A (2010) Quantitative determination of biogenic volatile organic compounds in the atmosphere using proton-transfer reaction linear ion trap mass spectrometry. *Analytical Chemistry*, **82**, 7952–7957.

Millar JG, Haynes KR (eds) (1998) *Methods in Chemical Ecology Vol. 1: Chemistry*. Kluwer, Dordrecht 391 pages.

Miresmailli S, Bradbury R, Isman MB (2010a) Qualitative assessment of an ultra-fast portable gas chromatograph (zNose (TM)) for analyzing volatile organic chemicals and essential oils in laboratory and greenhouses. *Arthropod-Plant Interactions*, **4**, 175–180.

Miresmailli S, Gries R, Gries G, Zamar RH, Isman MB (2010b) Herbivore-induced plant volatiles allow detection of *Trichoplusia ni* (Lepidoptera: Noctuidae) infestation on greenhouse tomato plants. *Pest Management Science*, **66**, 916–924.

Monson RK, Lerdau MT, Sharkey TD, Schimel DS (1995) Biological aspects of constructing volatile organic coumpund emission inventories. *Atmospheric Environment*, **29**, 2989–3002.

Monson RK, Trahan N, Rosenstiel TN *et al*. (2007) Isoprene emission from terrestrial ecosystems in response to global change: minding the gap between models and observations. *Philosophical Transactions Series A, Mathematical, Physical, and Engineering Sciences*, **365**, 1677–1695.

Nemecek-Marshall M, Macdonald RC, Franzen JJ, Wojciechowski CL, Fall R (1995) Methanol emission from leaves (enzymatic detection of gas-phase methanol and relation of methanol fluxes to stomatal conductance and leaf development). *Plant Physiology*, **108**, 1359–1368.

Owen SM, Harley P, Guenther A, Hewitt CN (2002) Light dependency of VOC emissions from selected Mediterranean plant species. *Atmospheric Environment*, **36**, 3147–3159.

Pangga IB, Hanan J, Chakraborty S (2011) Pathogen dynamics in a crop canopy and their evolution under changing climate. *Plant Pathology*, **60**, 70–81.

Pare PW, Tumlinson JH (1999) Plant volatiles as a defense against insect herbivores. *Plant Physiology*, **121**, 325–332.

Pasquill F (1950) Some further considerations of the measurement and indirect evaluation of natural evaporation. *Quarterly Journal of the Royal Meteorological Society*, **76**, 287–301.

Pattey E, Edwards G, Strachan IB, Desjardins RL, Kaharabata S, Riddle CW (2006) Towards standards for measuring greenhouse gas fluxes from agricultural fields using instrumented towers. *Canadian Journal of Soil Science*, **86**, 373–400.

Penuelas J, Llusia J (2004) Plant VOC emissions: making use of the unavoidable. *Trends in Ecology & Evolution*, **19**, 402–404.

Penuelas J, Staudt M (2010) BVOCs and global change. *Trends in Plant Science*, **15**, 133–144.

Perera RM, Marriott PJ, Galbally IE (2002) Headspace solid-phase microextraction–comprehensive two-dimensional gas chromatography of wound induced plant volatile organic compound emissions. *The Analyst*, **127**, 1601–1607.

Pio CA, Silva PA, Cerqueira MA, Nunes TV (2005) Diurnal and seasonal emissions of volatile organic compounds from cork oak (*Quercus suber*) trees. *Atmospheric Environment*, **39**, 1817–1827.

Sakulyanontvittaya T, Duhl T, Wiedinmyer C *et al*. (2008) Monoterpene and sesquiterpene emission estimates for the United States. *Environmental Science & Technology*, **42**, 1623–1629.

Schaub A, Blande JD, Graus M, Oksanen E, Holopainen JK, Hansel A (2010) Real-time monitoring of herbivore induced volatile emissions in the field. *Physiologia Plantarum*, **138**, 123–133.

Sharkey TD, Wiberley AE, Donohue AR (2008) Isoprene emission from plants: why and how. *Annals of Botany*, **101**, 5–18.

Shiojiri K, Karban R (2006) Plant age, communication, and resistance to herbivores: young sagebrush plants are better emitters and receivers. *Oecologia*, **149**, 214–220.

Simpson JR, McPherson EG (2011) The tree BVOC index. *Environmental Pollution*, **159**, 2088–2093.

Singsaas EL, Lerdau M, Winter K, Sharkey TD (1997) Isoprene increases thermotolerance of isoprene-emitting species. *Plant Physiology*, **115**, 1413–1420.

Somerville C, Youngs H, Taylor C, Davis SC, Long SP (2010) Feedstocks for lignocellulosic biofuels. *Science*, **329**, 790–792.

Stull RB (1988) *An Introduction to Boundary Layer Meteorology*. Kluwer Academic Publishers, Dordrecht, Boston, London, pp. xii + 666.

Tarvainen V, Hakola H, Hellen H, Back J, Hari P, Kulmala M (2005) Temperature and light dependence of the VOC emissions of Scots pine. *Atmospheric Chemistry and Physics*, **5**, 989–998.

Tilman D, Hill J, Lehman C (2006) Carbon-negative biofuels from low-input high-diversity grassland biomass. *Science*, **314**, 1598–1600.

Warneke C, Luxembourg SL, De Gouw JA, Rinne HJI, Guenther AB, Fall R (2002) Disjunct eddy covariance measurements of oxygenated volatile organic compounds fluxes from an alfalfa field before and after cutting. *Journal of Geophysical Research D Atmospheres*, **107**, 4067–4077.

Yuan JS, Himanen SJ, Holopainen JK, Chen F, Stewart CN Jr (2009) Smelling global climate change: mitigation of function for plant volatile organic compounds. *Trends in Ecology and Evolution*, **24**, 323–331.

Zeri M, Anderson-Teixeira KJ, Hickman GC, Masters M, Delucia EH, Bernacchi CJ (2011) Carbon exchange by establishing biofuel crops in Central Illinois. *Agriculture, Ecosystems and Environment*, **144**, 319–329.

Supporting Information

Additional Supporting Information may be found in the online version of this article:

Appendix S1. Major volatile compounds emitted from miscanthus (MXG), switchgrass (SW), and prairie plants (PRG) collected in closed chambers.

Please note: Wiley-Blackwell are not responsible for the content or functionality of any supporting materials supplied by the authors. Any queries (other than missing material) should be directed to the corresponding author for the article.