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A B S T R A C T

Significant amounts of ethanol are produced from biofuel crops such as corn and, in the future, likely switchgrass. The atmospheric effects of growing these plant species on a large scale are investigated here by measuring the plant-atmosphere exchange of volatile organic compounds (VOCs). Field grown corn and switchgrass emit VOCs at flux rates of 4.4 $nmol_C$ m^{-2} s^{-1} (10^{-9} mol carbon per square meter leaf area per second) and 2.4 $nmol_C$ m^{-2} s^{-1}, respectively. Methanol contributes ~60% to the molar flux but small emissions of carbonyls, aromatic compounds and terpenoids are relatively more important for potential air quality impacts. Switchgrass can act as a sink for carbonyls and aromatic compounds with compensation points of a few hundred pptv. In switchgrass moderate drought stress may induce enhanced emissions of monoterpenes, carbonyls and aromatics. Per liter of fuel ethanol produced, the estimated VOC emissions associated with the biomass growth of corn (7.8 g l^{-1}) or switchgrass (6.2 g l^{-1}) are in the same range as the VOC emissions from the use of one liter gasoline in vehicle engines. VOC emissions from the growing of biofuel crops can therefore be a significant contributor to the VOC emissions in the life cycle of biofuels. The VOC emissions from corn and switchgrass are small compared to those of tree species suggested as biofuel crops. Due to their reactivity with respect to OH the emissions from corn and switchgrass are not likely to have a significant impact on regional ozone formation.

1. Introduction

Over the last two decades, various legislation in the United States (U.S.) has targeted a reduction of the emissions of air pollutants to improve the air quality in cities, and a reduction of the country's dependence on (imported) petroleum. As one result the U.S. has become the world's largest producer of fuel ethanol. In the U.S. fuel ethanol is largely produced from corn grain in conventional starch-based fermentation. In 2010 more than 50 billion liter fuel ethanol were produced (EIA, 2011) consuming about 40% of the total annual corn harvest, which was grown on 35.7 Mha of agricultural land (NASS, 2011). The Renewable Fuel Standard (RFS) demands not only the production and use of certain amounts of renewable transportation fuels but is also phasing in set amounts of cellulosic fuel ethanol; by 2022 it requires that over 60 billion liters out of 136 billion liters renewable fuel are being produced from cellulosic feedstock. Switchgrass (*Panicum virgatum* L.) – a perennial grass native to North America – has a high net energy yield (Schmer et al., 2008), which makes it an attractive potential feedstock for cellulosic biofuel production on an industrial scale.

Plants produce numerous organic compounds in their metabolism, some of which are volatile and can escape into the atmosphere. Volatile organic compounds (VOCs) in the atmosphere are photo-oxidized and have the potential to enhance ozone production in polluted air and contribute to the organic aerosol fraction. Plants can also take up VOCs (Beattie and Seibel, 2007; Jardine et al.,

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2011; Karl et al., 2010; Kesselmeier, 2001; Keymeulen et al., 1993; Ugrekhelidze et al., 1997) and thereby remove them from the photo-oxidation cycle.

Despite the significance of corn as a food crop and more recently as an energy crop there are very few studies that quantified corn VOC emission rates. Lamb et al. (1987) compiled VOC emission rates from corn, and they use unpublished enclosure data from Zimmerman and co-workers (no isoprene, no α-pinene, 2.0 μg g_{dwt}^{-1} h^{-1} [microgram per gram biomass dry weight per hour] of other VOCs) for their biogenic non-methane hydrocarbon (NMHC) inventory. Lamb et al. (1993) cite corn emission data by Winer and co-workers and state that these findings show much lower emissions than those previously assumed. Lamb et al. (1993) indicate that there is a need for further measurements and suggest using half of the initially suggested emission rate for corn (1.1 μg g_{dwt}^{-1} h^{-1}) until the discrepancy is solved and assumed following composition: isoprene 0%; monoterpenes 20%; other VOCs 80%. The peer-reviewed work by Winer and co-workers regarding the emission rates of VOCs from vegetation (Winer et al., 1992) does not contain original numbers for corn emission fluxes but instead cites low isoprene emissions found by Evans et al. (1982) and results by Flyckt and co-workers that isoprene was not emitted in significant amounts by corn, but compounds eluting in the monoterpene region were the major emissions (Winer et al., 1992). In 1995 Das et al. measured VOC fluxes over a young corn field and estimated an emission rates of ~35 μg g_{dwt}^{-1} h^{-1} for methanol and ~47 μg g_{dwt}^{-1} h^{-1} of VOCs in total concluding corn could be a much more important VOC emitter than initially thought (Das et al., 2003). The scientific knowledge of the VOC emissions from intact switchgrass is limited to one laboratory study showing that emission rates of methanol, acetaldehyde, acetone, isoprene and monoterpenes are low (Eller et al., 2011). Simulated harvest by cutting and drying the switchgrass showed strongly enhanced VOC emissions and Eller et al. estimated the annual VOC emissions from a switchgrass field to be 6.4 kg C ha^{-1} yr^{-1}.

In this study VOC flux rates of field grown switchgrass were measured for the first time. VOC emission rates from corn complement the scarce data in the literature to improve the inventories of this important crop. This paper compares the VOC emissions of these two biofuel crops relative to the ethanol produced from the respective feedstock, and it analyses the relative importance of the VOCs in the composition for potential air chemistry impacts.

2. Material and methods

2.1. Field site

The experiments were carried out on Colorado State University's (CSU) horticultural farm (latitude 40.61°N, longitude 104.99°W, elevation 1526 m above sea level) in Fort Collins, Colorado, USA. Meteorological data was collected by a weather station collocated at the farm and data for 2010 are available online.[1]

The experiments on switchgrass were carried out on 7 days in 2010, September 13–15, 17 and on September 21–23 and corn was measured on September 19 and 20. The first four experimental days were sunny and warm with an average temperature of 17.6 °C and a maximum temperature of 30.9 °C (Table 1). The average relative humidity was 45% and these days were preceded by a warm and dry period. On September 18 the first of a series of frontal systems passed through with colder weather (T_{max} = 15 °C), an average relative humidity of 86% and small amounts of precipitation. September 19 and 20, the two measurement days for corn, were warm again (T_{max} = 31.0 °C) with passing clouds in the afternoon and some rain in the evening of the 20th. The last three days of switchgrass measurements were cooler again with an average temperature of 15.4 °C and small amounts of precipitation in evenings of the 22nd and 23rd. For the purpose of comparing the influence of weather and weather history on the VOC exchange of switchgrass the data collected on the first four days were separated into subset SG1 (N = 13), the data collected on the last three days were separated into subset SG2 (N = 21).

Table 1
Meteorological parameters during the VOC emission measurements of switchgrass (SG) and corn indicating that the first four days of SG measurements (SG1) were sunnier, warmer and drier than the days after September 18.

Day of month Sept 2010	Experimental period	T_{min} [°C]	T_{avg} [°C]	T_{max} [°C]	rH_{avg} [%]	$Precip_{cum}$ [mm]	$SolarRad_{avg}$ [a.u.]
13, 14, 15, 17	SG1	5.3	17.6	30.9	45	0	511
18	n/a	4.2	10.3	15.1	86	<0.25	212
19, 20	Corn	2.4	16.9	31.0	58	0.25	425
21, 22, 23	SG2	4.8	15.4	25.1	65	0.76	365
12–17	n/a	5.3	17.0	30.9	45	0	510
18–23	n/a	2.4	15.1	31.0	66	1.0	359

2.2. Plant material

Two switchgrass (*P. virgatum*) varieties — Blackwell and Pathfinder — were grown in plots of 5 by 10 m, three plots per variety. Switchgrass had been planted in 2008 and was in its 3rd growth season. Average yields of dry plant matter in 2009 were 10.7 Mg ha^{-1} and 10.0 Mg ha^{-1} for Blackwell and Pathfinder, respectively, and in 2010 the yields were 11.7 Mg ha^{-1} and 10.6 Mg ha^{-1}. Switchgrass was minimally irrigated to avoid serious drought stress. It received a total of 144 mm irrigation between June and September 2010 adding to 263 mm of cumulated precipitation (by September 23). Total precipitation in 2010 was 310 mm.

Two corn (*Zea mays*) cultivars — Jubilee sweet corn and the field corn variety Pioneer P0125XR — were planted on July 13, 2010 at a density of 32,000 plants per acre (12,950 plants per ha) and with a row distance of 30 inches (0.76 m). The two cultivars were grown in alternate rows. The no-till corn was irrigated with 1.5 inch (38 mm) of water per week and had received 381 mm irrigation by September 20.

2.3. Leaf cuvette

Leaves of corn and switchgrass plants were enclosed in the leaf cuvette of a portable photosynthesis system (Li-6400; LI-COR Lincoln, Nebraska, USA) with a 2 cm × 3 cm aperture. Two infrared gas analyzers (IRGA) located in the cuvette head measure sample and reference concentrations of CO_2 and H_2O for gas exchange calculations. The Li-6400 allows for controlling environmental parameters such as photosynthetic active radiation (PAR), leaf temperature and CO_2 concentration. The integrated light source provided intensities in the light saturation regime (≥1000 μmol photons m^{-2} s^{-1}), leaf temperature was kept at 30 °C, and a CO_2 concentration of 385 ppmv was maintained. Humidified synthetic air (ultra pure air; Scott Marrin, Inc., Riverside, California, USA) was provided to the air inlet of the Li-6400 console with about 70 μmol s^{-1} overflow, which was vented through a tee-union and 40 cm of 1/8″ (3.175 mm) Teflon tubing. Air (400 μmol s^{-1}) entered the leaf chamber where it was well mixed and analyzed by the

[1] Web data last accessed on September 30, 2011 at http://www.ncwcd.org/WeatherData/101_10.txt.

sample IRGA. Sample air for VOC analysis was taken at a flow rate of about 145 μmol s^{-1} through 8 m of 1/8″ Teflon tubing from a tee-union introduced into the tubing that connects both IRGAs in match mode.

2.4. PTR-MS

Proton transfer-reaction mass spectrometry (PTR-MS) was used for online VOC quantification; the working principle and fields of application can be found elsewhere (Blake et al., 2009; de Gouw and Warneke, 2007; Lindinger et al., 1998). The PTR-MS instrument was mounted on the back of a pickup truck to get as close as possible to the individual switchgrass and corn plots. The PTR-MS instrument monitored 26 VOC mass channels for one second each and a number of primary ion masses and analog inputs resulting in a cycle period of about half a minute (see Appendix B for mass list and data treatment). Instrumental backgrounds were determined by passing sample air through a catalytical converter. The instrument was calibrated in the field with a VOC standard (gas cylinder with 10 different VOCs in N_2 in low ppmv range) that was dynamically diluted into scrubbed air. For VOCs that were not represented in the gas standard sensitivities were estimated (Appendix B). VOC volume mixing ratios (VMR) were calculated according to de Gouw et al. (2003).

2.5. Bulk proportion of switchgrass and specific leaf area

After each VOC sampling the approximate portion of the leaf that was in the cuvette was cut out. For each leaf sample the one sided surface area was determined and leaf samples were dried in an oven at 50 °C for three days. Specific leaf areas (SLA; one sided leaf area in cm^2 over dry weight in g) were 133.2 cm^2 g^{-1} and 273.1 cm^2 g^{-1} for switchgrass and corn, respectively. On September 24, 2010 switchgrass was collected from each of the six plots. Stems and leaves were separated and dried in an oven at 50 °C for three days. Ratios between dry weight of stems and leaves in the bulk were 1:1 and very similar in all six plots.

2.6. Data collection and data treatment

A total of 34 switchgrass replicates and 18 corn replicates were measured. Nine corn replicates came from field corn, the other nine from sweet corn. For switchgrass eight sub-datasets were defined by meteorological differences of the measurement periods and by the two varieties measured as summarized in Table 2. As the width of the switchgrass leaves is smaller than the size of the leaf cuvette, two to three well-developed switchgrass leaves were lined up carefully to fill the 6 cm^2 aperture of the cuvette completely without overlapping. Mature corn leaves were put into the enclosure without clamping the central vein. For all replicates measurements from the empty cuvette (blanks) were taken prior to each sample. The collection of pairs of blanks and sample measurement was important since blank VMRs of VOCs varied from replicate to replicate and it allowed for more comprehensive statistical testing. Photosynthesis rate and stomatal conductance were followed on the screen of the Li-6400 and typically stabilized within 10–15 min of incorporation. Methanol concentration was also followed online, and incorporation time and time of approximate steady state were noted. This information along with visual inspection of the time series of methanol, acetone and acetaldehyde were used to define steady state periods for each replicate.

Table 2
Number of switchgrass replicates for the two experimental periods, for the two switchgrass varieties – Blackwell (B) and Pathfinder (P) – and the totals of the respective subsets of data.

		Variety		
		B	P	All
Period	SG1	8	5	13
	SG2	10	11	21
	All	18	16	34

Average and standard deviation of photosynthesis rate, stomatal conductance and leaf temperature were calculated for each replicate for the respective steady state period. VOC fluxes for each replicate were derived from concentration differences between steady state and blank, and from the flow rate of air through the cuvette; they were corrected for dilution due to transpiration. For each replicate this concentration difference was tested for significance using two-tailed t-statistics essentially testing for individual significant flux values ($p < 0.01$). Each replicate with a significant flux for a given VOC added one 'emission score' to that VOC if the flux was positive or one 'uptake score' if the flux was negative. At this significance level the probability of having more than one false-positive score (out of ≤34) is less than 0.05 and the test is still quite sensitive. As discussed below, this score system proved particularly useful for identifying VOCs with bidirectional flux character.

VOC concentration differences between steady state and blank were also tested for a number of sub-datasets (sweet corn, field corn, and all corn pooled; see Table 2 for switchgrass subsets) applying a paired *t*-test to identify whether a compound showed on average a significant flux in the respective sub-dataset. This test complements the flux scores in that way that even if very few individual replicates show a flux of a certain VOC above detection limit the test on pairs of steady state and blank measurements over a number of replicates is very sensitive to a flux if that VOC has a general tendency to be emitted or taken up, respectively.

Differences of average photosynthesis rate, stomatal conductance and VOC fluxes between field corn and sweet corn were tested using two-tailed t-statistics; differences between SG1 and SG2 and differences between corn and SG2 (all of those measurements were performed after September 18) were tested and treated in the same way.

Linear regressions of VOC fluxes versus VOC blank concentrations were calculated compiling *p*-value, slope, *y*-axis and *x*-axis intercepts and the coefficient of determination (R^2). Only those cases with *p*-values smaller than 0.05 were considered for the discussion. All statistical tests and descriptive statistics calculations were performed using IGOR pro Version 6 (WaveMetrics, Inc., Lake Oswego, Oregon, USA) with algorithms based on Zar (1999).

3. Results

3.1. Average leaf level trace gas exchange of switchgrass and corn

Fig. 1 shows the VOC emissions from corn and switchgrass (SG2 only). It depicts the averages of leaf level flux rates of compounds that are significantly emitted or taken up along with the significance levels of the plant species related flux differences. For reference, stomatal conductance (g_s) and net CO_2 assimilation rate (a) are included in this graph. Flux rates of corn are generally larger for all compounds compared to switchgrass. Conductance and assimilation rate of corn were more than three times those of switchgrass. VOC fluxes add up to 4.4 nmol of carbon per square meter leaf area per second ($nmol_C$ m^{-2} s^{-1}) and 2.4 $nmol_C$ m^{-2} s^{-1} for corn and switchgrass, respectively. (Note that VOC flux rate in $nmol_C$ m^{-2} s^{-1} is calculated from the molar VOC flux in nmol m^{-2} s^{-1} times the number of carbon atoms in the molecule. VOC flux rate in $nmol_C$ m^{-2} s^{-1} allows for direct comparison with net assimilation [see Discussion]; for all other purposes, tables and

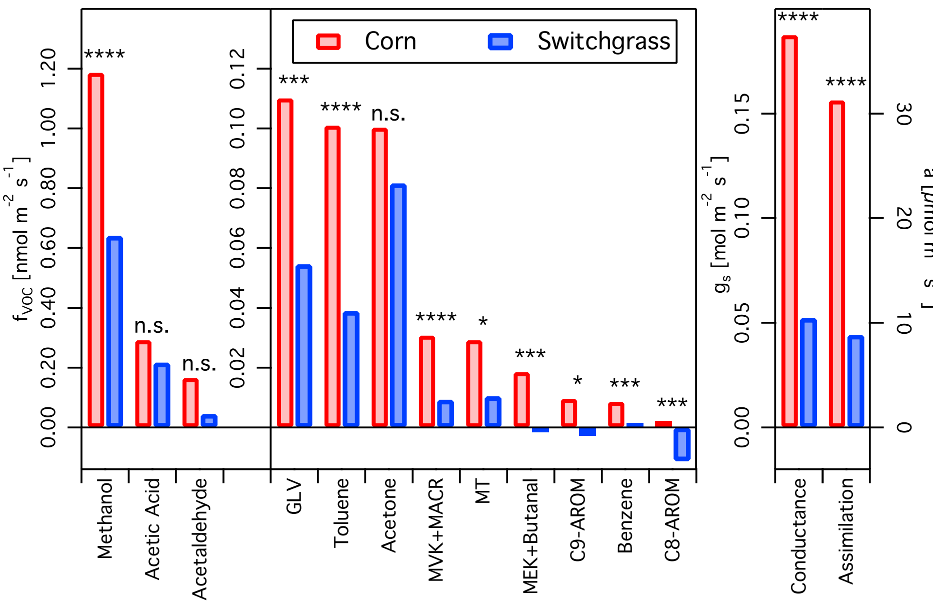

Fig. 1. VOC flux rates (f_{VOC}), stomatal conductance (g_s) and net assimilation rate (a) of corn and switchgrass. Bar height shows the average flux rate, the significance level of the plant species related flux differences are indicated by symbols (****$p < 0.001$; ***$p < 0.005$; **$p < 0.01$; *$p < 0.05$; n.s. not significant). Abbreviations: GLV … green leaf volatiles, also referred to as wound compounds; MVK … methy-vinyl-ketone (3-buten-2-one); MACR … methacrolein (2-propenal); MT … sum of monoterpenes ($C_{10}H_{15}$); MEK … methyl-ethyl-ketone (2-butanone); C9-AROM … sum of aromatic compounds with 9 carbons (C_9H_{12}); C8-AROM … sum of aromatic compounds with 8 carbons (C_8H_{10}). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

figures we use the molar based unit). In both species methanol is the dominant VOC emission contributing about 60% to the total quantified VOC flux on a molar basis (~30% on carbon basis). Acetic acid, green leaf volatiles (GLV), and toluene each add about 15% to the total VOC carbon flux from corn, whereas in switchgrass 21% of the VOC carbon flux stem from acetic acid and about 15% each come from GLV, acetone, and toluene. Methanol leaf level emission rates are on average 47% higher ($p < 0.005$) in field corn compared to sweet corn (Table A1) and 55% higher in Blackwell compared to Pathfinder (Table A2). The two cultivars of each species show no significant difference in conductance, assimilation, or in any other VOC flux rate averages (Tables A1 and A2). Therefore the data were pooled into ‘corn’ and ‘switchgrass’ for further considerations.

Corn and switchgrass show leaf level emissions of methanol, acetic acid, acetone, GLVs, toluene, monoterpenes (MT) and methyl-vinyl-ketone plus methacrolein (MVK + MACR) that are significantly ($p < 0.001$) different from zero (Tables A1 and A2). Each of these compounds has two or more emission scores, which indicates emission behavior, and less than two uptake scores. Corn also shows small but significant emissions of benzene ($p < 0.001$; 4 emission scores) and C9-aromatics ($p < 0.05$; 2 emission scores) neither of which are significant in switchgrass. On the other hand switchgrass shows a very small but significant uptake of C8-aromatics ($p < 0.005$; 7 uptake scores) whereas corn shows no significant flux for these compounds. Acetaldehyde shows both emission scores and uptake scores for both corn and switchgrass. In both plant species the average acetaldehyde flux rates are significantly ($p < 0.05$) positive (i.e. emission) and the magnitude is comparable to those of acetone; the bidirectional character of the acetaldehyde flux results in decreased significance levels for the calculated average fluxes, which will be discussed in 3.3. The sum of methyl-ethyl-ketone and butanal (MEK + butanal) shows a small but significant average emission rate in corn ($p < 0.001$), but a strong bidirectional character in switchgrass (see 3.2 and 3.3 for more details). Mass 57 was not identified but assuming a sensitivity of 20 ncps ppbv^{-1} (normalized ion counts per second per ppbv; see Appendix B) it has emission rates in the range of the C4 carbonyls for both corn and switchgrass. Methyl salicylate (MeSA; $MH^+ = 153$ m/z) and methyl jasmonate (MeJA; $MH^+ = 225$ m/z) are semi-volatile stress markers (Karl et al., 2008) and emissions of MeSA were very small for both plant species; no fluxes of MeJA were detected.

3.2. Influence of weather history on VOC flux rates of switchgrass

Due to modest but carefully timed irrigation the switchgrass did not suffer from any visible drought stress. Fig. 2a shows, however, that the 13 replicates before September 18th (SG1) have significantly ($p < 0.001$) lower stomatal conductance in comparison to the 21 replicates (SG2) measured after the cooler and moist period even though leaf temperature and PAR in the cuvette were the same for all replicates. This indicates that weather history has an influence on the physiology of switchgrass. Flux rates of methanol (Fig. 2b) where higher for SG1 than for SG2 ($p < 0.005$) following the pattern of stomatal conductance. A linear regression ($p < 0.001$) between methanol and conductance (Fig. 3, top panel) reveals that 36% of the variability of the methanol flux rate can be explained by stomatal conductance. Most of the other VOCs were higher at low conductance, suggesting that their release may be associated with stress induced by hot and dry weather. The bottom panel of Fig. 3 shows that mass 47 fluxes decrease strongly with increasing conductance. Formic acid and ethanol both contribute to this ion signal; see Appendix B for details on quantification of both. The increased mass 47 flux rates occur predominantly in SG1 with 11 emission scores out of 13 replicates compared to 6 emission scores (and 2 uptake scores) out of 21 SG2 replicates (Table A3). Also monoterpenes, MVK + MACR, MEK + butanal, and C9-aromatics (Fig. 2c–f) had higher flux rates for SG1 than for SG2 ($p < 0.05$). Pathfinder showed a tendency to be more susceptible to stress induced VOC emission (Fig. 2) but only 5 replicates of Pathfinder in SG1 and generally different numbers of replicates in the sub-data groups (Table 2) inhibit a detailed analysis of variances.

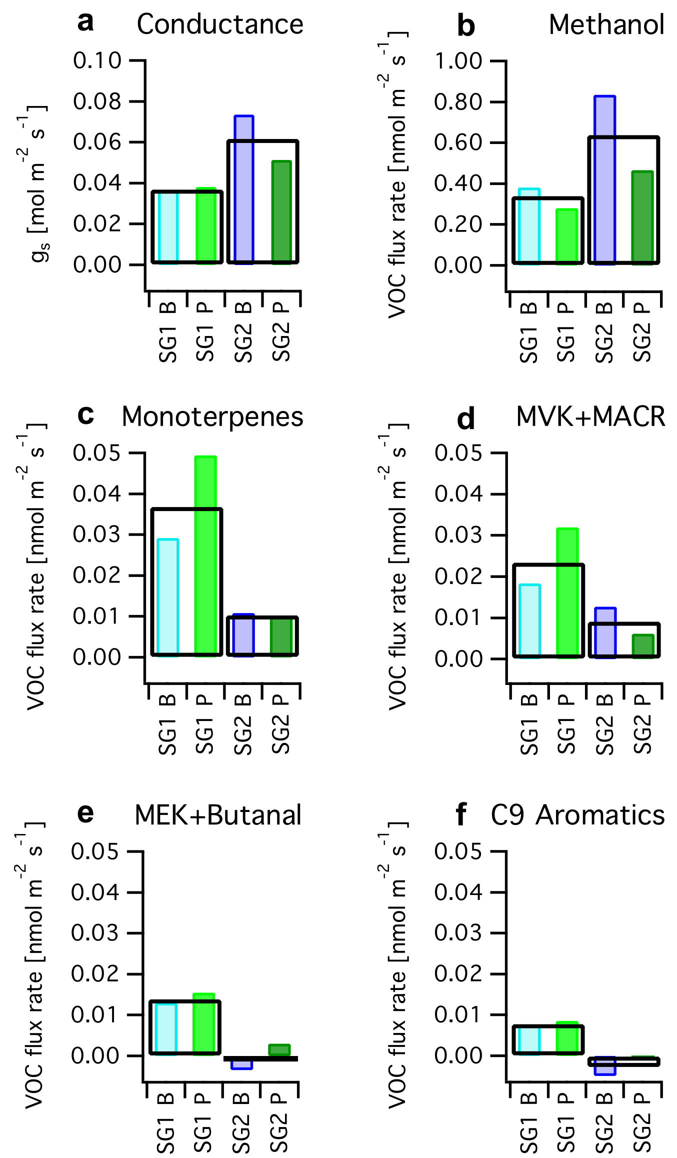

Fig. 2. a) Average stomatal conductance and average VOC flux rates (b–f) of the two-by-two categories of switchgrass measurements (SG1 = period 1 “dry”; SG2 = period 2 “moist”; B = Blackwell; P = Pathfinder) as filled bars and the respective averages for period 1 and period 2 with data from both varieties combined as broad hollow black bars.

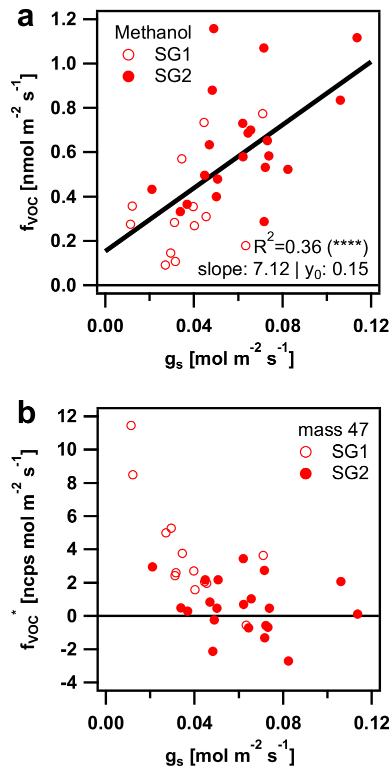

Fig. 3. Methanol flux rates (top panel) and flux rate equivalents at mass 47 (bottom panel) versus stomatal conductance (g_s) with hollow and solid markers for SG1 and SG2 period, respectively. Top panel includes results of the linear regression (all SG combined).

3.3. *VOC uptake and bidirectional exchange*

Even with an empty cuvette, the levels of certain VOCs were above detection limit, due to the outgassing of leaf cuvette materials, memory effects and impurities in the water bubbler that humidified the synthetic air. The blank VMRs in these experiments were low, few hundred pptv (pmol mol^{-1}) or lower for most VOCs. It was found that the levels of some of these VOCs actually influenced the leaf-level fluxes. For example, Fig. 4 shows scatter plots and regressions between the VOC flux rates of switchgrass and the VMR of C9-aromatics, C8-aromatics, toluene, MEK + butanal, and MVK + MACR in the empty cuvette (blank; measured immediately before each individual replicate). VOC flux rates of the compounds shown in Fig. 4 were small in comparison to methanol. *P*-values of the regressions were smaller than 0.005 identifying the regressions as statistically very significant. Determination coefficients (R^2) were between 0.44 and 0.29, which is reasonable considering that these flux rates are close to or below the flux detection limit of the system. The *x*-axis intercepts suggest compensation points of 210 pptv, 140 pptv, 360 pptv, 160 pptv, and 290 pptv for C9-aromatics, C8-aromatics, toluene, MEK + butanal, and MVK + MACR, respectively. At ambient VMRs below the compensation point the leaf acts as a source of the respective VOC, at higher VMRs as a sink. Consequently switchgrass may act as source or as sink for all five of the VOCs above depending on ambient VMRs. Acetaldehyde flux rates of switchgrass and of corn were clearly bidirectional (Table A2) but *p*-values of 0.1 and 0.8, respectively, indicate that in this study linear regression is not a reliable model for acetaldehyde; no compensation points can be deduced. The determination of compensation points was not a focus of these measurements and should be studied in more detail.

4. Discussion

4.1. *Corn and switchgrass compared to literature and other biofuel crops*

VOC emissions from switchgrass and corn have a similar VOC composition and emission rates at light saturation and 30 °C of both C4 plant species are in the same order of magnitude. For both switchgrass and corn methanol is the VOC with the strongest emission rates, which is in line with the findings for intact plants or ecosystems of other graminoids (Bamberger et al., 2010; Brunner et al., 2007; Fukui and Doskey, 1998; Hörtnagl et al., 2011; Kirstine et al., 1998; Ruuskanen et al., 2011). Total VOC emission rates are somewhat higher for corn than for switchgrass. Compared to woody biofuel crops the emission rates are generally small (Graus et al., 2004; Isebrands et al., 1999; Kesselmeier, 2001;

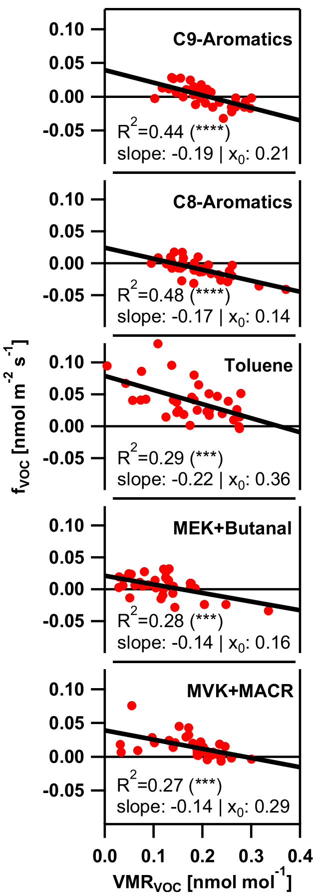

Fig. 4. Switchgrass VOC flux rates versus blank cuvette VMRs with results of linear regressions including *x*-axes intercept (x0).

Kesselmeier and Staudt, 1999; Winters et al., 2009). The ratio of carbon loss due to VOC emission over net carbon uptake (assimilation) is 0.014% and 0.027% for corn and switchgrass, respectively, which shows the economic use of fixed carbon in these C4 plants.

Lamb et al. (1987) assumed a total VOC emission rate for corn of 2.0 μg g_{dwt}^{-1} h^{-1} (0% isoprene; 0% α-pinene; 100% other NMHC) in their inventory of biogenic hydrocarbon emissions, but due to discrepancy of the scarce experimental data available at the time (and to date) the authors halved these VOC emission rates in an inventory update and used 1.1 μg g_{dwt}^{-1} h^{-1} and a composition of 0% isoprene, 20% monoterpenes and 80% other VOCs instead (Lamb et al., 1993). Our results confirm that monoterpenes (this study 0.39 μg g_{dwt}^{-1} h^{-1}) do get emitted, but monoterpene emission rates and the total VOC emission rate of corn (this study 9.68 μg g_{dwt}^{-1} h^{-1}) appear to be underestimated in their inventory. Das and co-workers estimated fluxes over a corn field in its early developmental stage (biomass of 100 g dry weight per m^2) of 3450, 425, 661 μg m^{-2} h^{-1} of methanol, acetone, and monoterpenes, respectively, using a gradient method (Das et al., 2003), and those fluxes measured at ~25 °C translate into emission rates of 34.5, 4.25, and 6.61 μg g_{dwt}^{-1} h^{-1}, respectively. The relative VOC composition in Das et al. (2003) is similar to the composition found in this study (3.74, 0.57, and 0.39 μg g_{dwt}^{-1} h^{-1} for methanol, acetone, and monoterpenes, respectively) but the emission rates in their study are an order of magnitude higher. This could indicate that corn emission rates of methanol, acetone and monoterpenes may be much higher in young plants (39 days after planting) than in further developed (68 days after planting) corn plants.

Switchgrass VOC emission rates of methanol, acetaldehyde, acetone, isoprene, and monoterpenes from this study are between 1.4 and 3.8 times higher than those published by Eller et al. (2011). In their study they used greenhouse grown, potted plants and performed the measurements in a plant chamber that averages over a whole plant and had a PAR flux of 400–600 μmol m^{-2} s^{-1}. Here flux rates were measured from field grown switchgrass under light saturation and only healthy looking leaves from the top of the canopy were put into the cuvette. This could be at least in part causing the differences.

4.2. Biofuel crop emissions per ethanol produced

To put the VOC emission rates in perspective, we normalized estimated annual emissions by the amount of ethanol produced from the respective feedstock (fuel yield normalized emission, FYNE, in grams of VOC emitted per liter ethanol produced). The absolute FYNE numbers should be seen as metric to compare VOC emissions associated with the growth of biofuel crops to other VOC emissions during the life cycle of biofuels and other energy sources. Due to the basic up-scaling approach (see Appendix A) uncertainties in this estimate cannot be strictly quantified, but the FYNE numbers are likely close to an upper limit. Details on the grain and biomass yields, growth season estimates and ethanol yields from grain alcohol production and cellulosic fermentation, respectively, are given in Appendix A. Fig. 5 lists FYNEs for the individual VOCs measured in this study. The feedstock growth results in the emission of 7.8 and 6.2 g l^{-1} (grams VOC per liter fuel ethanol produced) from corn and switchgrass, respectively. Corn has a slightly higher total FYNE than switchgrass mostly due to the higher methanol emission rate, which is the single most dominant FYNE contributor for both plant species. The FYNE of corn only takes the fuel production from kernels into account. For corn, residue to crop ratio is about 1:1. Depending on agricultural practice 40%–70% of the corn stover could be collected (Sheehan et al., 2003). Utilizing corn stover for cellulosic ethanol production would add to the ethanol yield from corn and thus reduce its FYNE.

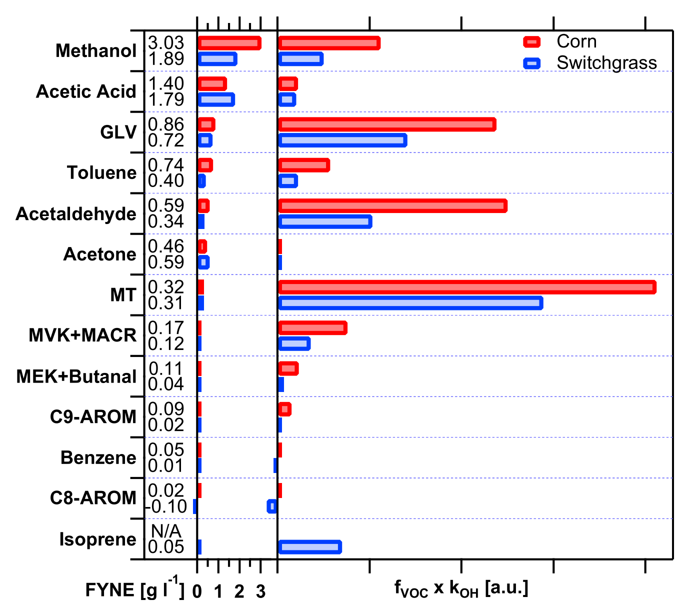

Fig. 5. Estimated annual VOC emissions from corn (top bars) and switchgrass (bottom bars) normalized to the ethanol yield of the respective crop (FYNE; fuel yield normalized emission) on the left. Potential air chemistry impact of the biofuel crop VOC emissions relative to the composition of VOCs on the right. Compound abbreviations as in Fig. 1 and in the text.

FYNEs of fuel ethanol from corn and switchgrass are in the same range as VOC emissions from the consumption of gasoline found in tunnel studies [4.6 g l^{-1} of non-oxygenated NMHC plus ethanol in 2000/2001 in Milwaukee, WI (Lough et al., 2005) and 9.1 g l^{-1} total VOC in 1993 in Los Angeles, CA (Fraser et al., 1998)]. This indicates that feedstock growth related VOC emissions can be a significant contribution to the total VOC emission over the life cycle of biofuels used in combustion engines. Here it should be mentioned that the source of VOCs from corn, switchgrass or other biofuel crops is distributed over large areas and these VOCs are emitted in mostly rural areas whereas tailpipe emissions are largely localized to cities and major traffic routes and co-emitted with large amounts of NO_x and other pollutants. An analysis of total VOC emissions in the whole life cycle of the ethanol production for fuel use is beyond the scope of this paper.

4.3. Air chemistry impact

VOC emissions from corn and switchgrass are dominated by methanol and acetic acid, which are not highly reactive in the atmosphere. The product of VOC flux rates with their respective OH reaction rate coefficients (Albaladejo et al., 2002; Atkinson and Arey, 2003; Atkinson et al., 2006) provides some insight into their relative importance for ozone formation. Fig. 5 shows that comparatively small emissions of reactive hydrocarbons, carbonyls and aromatics dominate the potential air chemistry impact over the less reactive main emissions. Other plant species that have been suggested as feedstock for biofuel production such as poplar, willow or eucalyptus emit isoprene and/or monoterpenes at much higher rates of tens of μg g_{dwt}^{-1} h^{-1} (Isebrands et al., 1999; Kesselmeier and Staudt, 1999; Winters et al., 2009). Monoterpene emission rates of corn and switchgrass found in this study are 0.39 μg g_{dwt}^{-1} h^{-1} and 0.13 μg g_{dwt}^{-1} h^{-1}, respectively, are small compared to the tree species. Ashworth et al. (2011) showed that isoprene emissions from short rotation coppice (SRC) may have an impact on regional surface concentrations of ozone and biogenic secondary organic aerosol (Ashworth et al., 2011). They chose scenarios at realistic magnitudes (18 Mha and 70 Mha of SRC in the USA and Europe, respectively) and the resulting increases in regional ozone concentrations were very small. Due to the much lower OH reactivities of the VOC emissions from corn and switchgrass it seems likely that they will not have any significant impact on regional ozone.

5. Conclusions

VOC emission rates of corn and switchgrass – both are C4 plants – the former being the dominant biofuel crop for fuel ethanol production in the USA and the latter being a potential feedstock for cellulosic biofuel production in the future, are small compared to those of woody plants. Switchgrass may even act as a sink for carbonyls and aromatic compounds at ambient mixing ratios of a few hundred pptv of those compounds. It is unlikely that VOC emissions from the growth of switchgrass or corn, even if planted on very large scales, contribute significantly to regional ozone formation, but the total amount of VOCs per liter ethanol produced emitted from the growth of the biofuel crops is in the same range as VOCs emitted by vehicles per liter gasoline used.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2011.12.042.

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