VOC emissions and carbon balance of two bioenergy plantations in response to nitrogen fertilization: A comparison of *Miscanthus* and *Salix*[☆]

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ABSTRACT

Energy crops are an important renewable source for energy production in future. To ensure high yields of crops, N fertilization is a common practice. However, knowledge on environmental impacts of bioenergy plantations, particularly in systems involving trees, and the effects of N fertilization is scarce. We studied the emission of volatile organic compounds (VOC), which negatively affect the environment by contributing to tropospheric ozone and aerosols formation, from *Miscanthus* and willow plantations. Particularly, we aimed at quantifying the effect of N fertilization on VOC emission. For this purpose, we determined plant traits, photosynthetic gas exchange and VOC emission rates of the two systems as affected by N fertilization (0 and 80 kg ha^{-1} yr^{-1}). Additionally, we used a modelling approach to simulate (i) the annual VOC emission rates as well as (ii) the OH· reactivity resulting from individual VOC emitted. Total VOC emissions from *Salix* was 1.5- and 2.5-fold higher compared to *Miscanthus* in non-fertilized and fertilized plantations, respectively. Isoprene was the dominating VOC in *Salix* (80 –130 μg g^{-1} DW h^{-1}), whereas it was negligible in *Miscanthus*. We identified twenty-eight VOC compounds, which were released by *Miscanthus* with the green leaf volatile hexanal as well as dimethyl benzene, dihydrofuranone, phenol, and decanal as the dominant volatiles. The pattern of VOC released from this species clearly differed to the pattern emitted by *Salix*. OH· reactivity from VOC released by *Salix* was ca. 8-times higher than that of *Miscanthus*. N fertilization enhanced stand level VOC emissions, mainly by promoting the leaf area index and only marginally by enhancing the basal emission capacity of leaves. Considering the higher productivity of fertilized *Miscanthus* compared to *Salix* together with the considerably lower OH· reactivity per weight unit of biomass produced, qualified the C$_4$-perennial grass *Miscanthus* as a superior source of future bioenergy production.

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1. Introduction

The assumed increased global energy demand in the future (International Energy Agency, 2011), the obvious scarcity of natural resources, as well as economic aspects will enforce the development of renewable energy technologies compared to usage of traditional fossil fuels (Chu and Majumdar, 2012; Moriarty and Honnery, 2012). Power generation from bioenergy crops is considered a remarkable renewable energy source (Bentsen and

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Felby, 2012) and European Community (EC) countries have stipulated biomass to account for 56% of renewable energy generation by 2020, corresponding to an increase in bioenergy generation from 3.8 EJ in 2005 to 10.0 EJ (Bentsen and Felby, 2012).

The cultivation of short rotation coppices (SRC) with fast growing woody plant species seems to be promising considering yield, energy output, economic and ecological aspects and, therefore, has high establishing potential in large areas of Europe (Ericsson et al., 2009; Gauder et al., 2012; Werner et al., 2012; Aust et al., 2014; Schweier et al., 2017). For such bioenergy plantations, SRC of willow (*Salix* spp.) or poplar (*Populus* spp.) are often recommended in Central Europe (Boehmel et al., 2008), because their woody biomass has better combustion properties than non-woody solid biofuels (Gauder et al., 2012). Besides SRC, perennial grasses with high growth potential are recommended for high-yield bioenergy plantation systems (Boehmel et al., 2008). The C_4-plant *Miscanthus* spp. is a promising species due to its high production capability in temperate regions (Lewandowski et al., 2000; Heaton et al., 2010; Gauder et al., 2012).

Despite positive reputation of bioenergy plantations in general, ecological assessments have highlighted potentially negative effects of some cropping systems (Rowe et al., 2009, 2013; Cherubini et al., 2011; Schweier et al., 2017). In particular, the emission of nitrous oxide (N_2O) is able to counteract the reduction of the global warming potential by C sequestration (Mosier, 1994). Triggered by application of N-fertilizer, N_2O emission may even overcompensate the effect of C sequestration (Crutzen et al., 2008) and it additionally worsens the greenhouse gas (GHG) balance of a given plantation system because of the high energy input needed for fertilizer production (Kongshaug, 1998; Schweier et al., 2017). Depending on the history of a plantation, also CO_2 release from the soil C stock can affect the GHG balance of such systems (Searchinger et al., 2008).

An additional environmental impact receiving more attention in the last years is the emission of volatile organic compounds (VOCs) (Ashworth et al., 2013; Graus et al., 2013). VOCs play an important role in air chemistry; depending on their hydroxyl radical (OH·) reactivity, they contribute to the formation of tropospheric ozone (Atkinson and Arey, 2003), and to aerosol formation, the latter counteracting global warming (Claeys et al., 2004). VOCs indirectly affect global warming by quenching atmospheric (OH·) concentrations thereby increasing the half-lifetime of atmospheric methane, whose degradation depends on the OH· availability (Pike and Young, 2009). Although thousands of different VOCs are emitted into the atmosphere by vegetation, the emission of isoprene is quantitatively of highest significance as it contributes about 44% to the total annual biogenic VOC emission of about 1150 Tg C (Guenther et al., 1995, 2012). Most woody species used in bioenergy plantations such as poplar, willow, oil palm and eucalypts are strong isoprene emitters and expanding the area of such plantations might have considerable impacts on regional air quality (Wiedinmyer et al., 2006; Ashworth et al., 2012, 2013; Copeland et al., 2012; Rosenkranz et al., 2015).

In the present study, we concentrate on the bioenergy plants *Miscanthus* and *Salix*. It is expected that these cropping systems will have a significant share of future's sustainable energy sources (Fischer et al., 2005; Styles et al., 2008). Both species can achieve high biomass yields in temperate climate zones (Price et al., 2004; Wilkinson et al., 2007; Boehmel et al., 2008; Gauder et al., 2012), but while willow is known as high isoprene emitter, *Miscanthus* is supposed to emit only minor amounts of less reactive VOCs (Copeland et al., 2012). However, emissions might change with fertilization, although the direction of the change has not been conclusively evaluated, since it depends on species and type of emission (Harley et al., 1994; Monson et al., 1994; Litvak et al., 1996;

Ormeño and Fernandez, 2012).

Investigations regarding the sensitivity of VOC emissions of *Salix* or *Miscanthus* to N fertilization have not been reported. In particular, the usual management of willow SRC involves fertilization (Jug et al., 1999), while *Miscanthus* is able to fix atmospheric nitrogen and, thus, requires low if any fertilizer input (Heaton et al., 2008; Rowe et al., 2009). The present study aims to narrow this gap by determining the emission of VOCs from *Miscanthus* and *Salix* at leaf and plantation level and, thus, to quantify the impact of N fertilization on these emissions. Moreover, by considering biomass increment, we aimed at estimating the potential C sequestration by these cropping systems. It was hypothesized that (i) *Miscanthus* is preferable over *Salix* plantations because of lower isoprene and other VOC emissions, hence, lower OH· reactivity, and that (ii) the application of fertilizer further enforces this difference due to enhanced isoprene emissions from *Salix*.

2. Materials and methods

2.1. Experimental site and field trial description

The field experiment was performed in Southwest Germany at the University of Hohenheim research station, Ihinger Hof (48.75°N and 8. 92°E, 480 m asl). Details of the field site are given in Gauder et al. (2012). In 2002, the experimental site with willow (*Salix schwerinii x viminalis* "Tora") and *Miscanthus* (*M. x giganteus*) plants was established (Boehmel et al., 2008). The trial was a complete split-plot design with main plots for the cropping system, which were replicated four times. These main plots were divided into two subplots with an area of 160 m^2 each with different N-application levels. Hence, every subplot was also four times replicated in total. Within each subplot, sampling was done with at least a 2 m buffer to the border. On the experimental plots, either 0 kg N ha^{-1} yr^{-1} or 80 kg N ha^{-1} yr^{-1} were applied annually as ammonium stabilized N-fertilizer (Entec26; K + S Nitrogen GmbH, Mannheim, Germany) which contained 7.5% nitrate-N, 18.5% ammonium-N, 13% sulphur and DMPP as N stabilizer. All other nutrients were held in optimum ranges. The agricultural treatments were in accordance to common cultivation practices. The *Miscanthus* plots were harvested each year in late winter or early spring. In 2010, the *Miscanthus* plots were harvested in March and fertilizer was lastly applied on the respective subplots on April 9th, 2010, before the new sprouts emerged. The *Salix* SRC was harvested in 2003, one year after planting. Afterwards the rotation time was three years. The last harvest was on February 2nd, 2009. Fertilizer was applied last on April 21st, 2010. No weed control was carried out in 2010 for both crops.

2.2. Plant biomass data determination

The planting density of the *Salix* coppice was 20,000 plants ha^{-1}. During our measuring campaign end of June 2010, the number of shoots per tree (n = 4) was counted and the shoots were distinguished into three classes according to height (*i.e.* small shoot: 0–2 m; middle shoot: 2–4 m; long shoot: 4–7 m). In the *Miscanthus* plots, plant density (ha^{-1}) was calculated annually by counting the number of shoots per m^2. For both species, shoot height of four plants was assessed (n = 4). Subsequently, the fresh leaves of every shoot were collected and their areas were determined using scanner (CanonScan Lide 70, Canon, Amsterdam, The Netherlands) and an image analyzer software (GSA Image Analyser, GSA GmbH, Rostock, Germany). The obtained leaves were oven-dried (60 °C, 48 h) and, thereafter, we determined the dry weights. From these data, mean leaf area, weight per plant and leaf area index and specific leaf weight per ha, as well as mean stand

height were calculated. Annual yield increment of *Miscanthus* and *Salix* plots were accounted and calculated after each harvest. Below-ground biomass of the two species was estimated according to literature information, assuming a shoot:root (S/R) ratio of 1.33 for *Miscanthus* (Beuch et al., 2000) and 1.75 for *Salix* (Heller et al., 2003). In addition, we assumed that the C content of below ground tissues was the same as in leaves (50%) (Rytter, 2012).

2.3. Plant C and N content and stable C and N isotope signatures

The $\delta^{13}C$ and $\delta^{15}N$ signatures as well as total C and N contents in leaves were determined in aliquots (1.5 mg) of dried leaf material. For this purpose, leaf material was weighed into tin capsules (IVA Analysentechnik, Meerbusch, Germany) and analyzed in an isotope ratio mass spectrometer (Delta plus, Thermo Finnigan MAT GmbH, Bremen, Germany) coupled to an elemental analyzer (NA 2500, CE Instruments, Milan, Italy) (Simon et al., 2010). A working standard (glutamic acid) was calibrated against the primary standards USGS 40 (glutamic acid $\delta^{13}C_{PDB} = -26.39$‰) and USGS 41 (glutamic acid $\delta^{13}C_{PDB} = 37.63$‰) for $\delta^{13}C$, and USGS 25 (ammonium sulphate, $\delta^{15}N_{Air} = -30.40$‰) and USGS 41 (glutamic acid $\delta^{15}N_{Air} = 47.60$‰) for $\delta^{15}N$ and analyzed after every tenth sample to account for a potential instrument drift over time (Simon et al., 2010).

2.4. Soil total N content determination

Soil sampling was conducted with a soil probe three times in every subplot to a depth of 90 cm at the end of March, 2010. The samples were divided into 0–30 cm, 30–60 cm and 60–90 cm depth, respectively. The three samples per soil depth within each subplot were merged to one composite sample for each soil depth. Soil samples were air-dried and sieved to 2 mm. Soil mineral N (N_{min}) concentration was determined by combustion (n = 4) (Vario Max CNTS, Elementar, Langenselbold, Germany) (Gauder et al., 2016).

2.5. Gas exchange measurements and sampling of volatiles

Gas exchange was determined in a height of 1–1.5 m on three mature sun leaves of each of four plants per treatment and species on the same plants (n = 4) used for biomass analysis (see above). Measurements were performed in June 2010, between 10 a.m. and 4 p.m. by using a portable gas exchange measurement system (GFS 3000, Walz, Effeltrich, Germany). To allow VOC emission measurements with the same system, original tubing was replaced by chemically inert perfluoralkoxy (PFA)-tubes. For measurements, intact leaves were placed into the 8 cm^2 leaf cuvette, which was flushed with ambient air at 650 µmol min^{-1}. Leaf temperature (30 °C), air humidity (10.000 ppm), CO_2 concentration (400 ppm) and light intensity (1000 µmol m^{-2} s^{-1}) were kept constant during the measurements. Following a 20 min adaptation period, net photosynthetic rate (P_N) and stomatal conductance (g_s) were analyzed. Intrinsic water use efficiency (iWUE) was calculated as the ratio between P_N and g_s. For determination of VOC emission rates, part of the air at the cuvette outlet was drawn over a T-piece onto glass tubes (Twister desorption liner, Gerstel GmbH & Co. KG, Mülheim, Germany) packed with adsorbent beds of 30 mg Tenax TA (60/80 mesh) and 40 mg Carbotrap (20/40 mesh) (Supelco, Bellafonte, PA) separated by silanized glass wool. Accumulation of VOCs occurred for 60 min at a flow rate of 100 ml min^{-1}. Empty cuvettes without leaves were analyzed in the same way for background correction. Immediately after sampling, the glass tubes were sealed, placed in an ice-filled container and stored at 4 °C until analysis.

2.6. VOC analysis

Volatiles were analyzed on a gas chromatograph (Model 7890A, Agilent, Germany) equipped with a thermodesorption/cold injection system (TDU-CIS) (Gerstel, Germany) and a mass-selective detector (5975C, Agilent, Germany). For this analysis, the glass tubes were heat desorbed at 240 °C, cryo-focused at −100 °C and, after heating the CIS to 240 °C, injected onto the separation column (DB-624, length 60 m, id. 0.25 mm, 1.4 µm film thickness, Agilent Technologies, Böblingen, Germany). The oven temperature program started at 40 °C, temperature was increased at a rate of 6 °C min^{-1} until 100 °C were reached, when the temperature ramp was speed up to 16 °C min^{-1} until 230 °C. The spectra of the NIST database and external standards of known concentration (isoprene, acetaldehyde and limonene) were used for peak identification and quantification, respectively. Quantification was done by using calibration factors of acetaldehyde for all oxygenated compounds, isoprene for hemiterpenes, and limonene for non-oxygenated compounds. Emission rates were calculated by subtracting VOC concentrations of the empty cuvette from plant cuvette concentrations and by accounting for the flow rate through the system and the leaf area.

2.7. Statistical analysis

All statistical analyses were performed using SPSS 21.0 (SPSS Inc., Chicago, IL, USA) and Sigmaplot 12.5 (Systat Software GmbH, Erkrath, Germany). For soil, plant gas exchange and growth pattern experiments, all statistical tests were based on four individual trees or shoots (n = 4, independent replications) for each (non-)fertilized treatment and/or species. For VOC emission experiment, the independent plant replications of each (non-)fertilized treatment and/or species are five (n = 5), except for the treatment of fertilization of *Miscanthus* (n = 4). Data were first tested by either Kolmogorov-Smirnov or Shapiro-Wilk tests for normal distribution. Non-normally distributed data were transformed using either log- or square-root transformation. Significant differences between two N fertilization treatments within each species and/or between two species within each (non-)fertilized treatment were assessed by using the unpaired Student's t-test. Differences were considered significant at $p < 0.050$. The VOC emission data were log transformed before being subjected to multivariate data analysis using principal component analysis (PCA) and PCA loadings plots in order to compare *Miscanthus* and *Salix* samples for VOC emission patterns. For this purpose, data were processed online using MetaboAnalyst 3.0 (http://www.metaboanalyst.ca) (Xia et al., 2015).

2.8. Simulation of plant development and VOC emission

We employed the process-based vegetation model Landscape-DNDC (Haas et al., 2013) with a strong biogeochemical component and a coupled VOC emission model to scale the measured emissions throughout the growth cycles in order to estimate the full GHG and VOC balance. For VOCs and GHG estimations we used the PSIM vegetation model (Grote et al., 2011) in combination with the 'Guenther' emission algorithm (Guenther et al., 1993, 1995) together with a phenological model accounting for dynamic seasonal changes of modelling parameters as described in Guenther et al. (1995, 2006) and Grote et al. (2010). Parameters other than standard emission rates are set according to Guenther et al. (1995).

The model system has been evaluated and applied for reproducing the development of poplar SRC under various environmental conditions (Werner et al., 2012; Schweier et al., 2017), but

has also been used for the simulation of grassland development (Grote et al., 2009). We ran the coupled model with weather (temperature, radiation, precipitation) data from 2002 to 2010 of the Ihinger Hof research station and initialized the run with measured soil properties, aiming to simulate a realistic development of *Miscanthus* and *Salix* and, at the same time, providing a pre-run (previous to the year 2010) avoiding errors provoked by imprecise initialization. Plantings, fertilization, cutting and harvesting were reproduced in the simulation as prescribed by management protocols and the parameters describing biomass and leaf area development, *i.e.* specific leaf area, height/diameter ratio, and maximum foliage biomass were calibrated with measurements from 2010. Phenological development (start and period length of leaf expansion) has been set according to observations at the field and to literature information (Hastings et al., 2009; Eckersten, 1994). In addition, we adjusted physiological parameter, *i.e.* specific respiration of tissue, carboxylase activity, to the measurements at the same site published by Gauder et al. (2012).

To provide a rough estimate of the likely global warming potential (GWP) per year and species, the simulation outputs were used to estimate the average C sequestration throughout an entire rotation cycle. For this purpose, the following assumptions were made: The plantation lifetime of both *Miscanthus* and *Salix* was set to 16 years; a reasonable estimate for both species (Lewandowski et al., 2000; Murphy et al., 2014). For *Salix* this included an initial cut after the first year and 5 subsequent cycles of 3 years each. Since the plantations were 9 years old during analysis, we extrapolated the yield for the years 10–16 assuming an unchanged performance based on the second rotation period for *Salix* and the years 5–9 for *Miscanthus*. In the model, C sequestration was assumed equal to net ecosystem production, considering photosynthetic fixation minus soil and plant respiration.

VOC emissions were calculated according to the same scheme. Emission factors (EF), which were assumed constant throughout the rotation, were directly derived from the gas exchange measurements. In the model, isoprene and other VOCs were treated separately, since isoprene emission rates were calculated in dependence on light and temperature, while the emission of other VOCs was assumed temperature dependent only. The measured emission rates (in ng m^{-2} s^{-1}) were converted to mass based emission factors (EF in µg C g^{-1} DW h^{-1}) considering the measured biomass-area relationship (for *Salix* EF$_{iso}$ = 66.9 and 99.9, EF$_{other}$ = 28.7 and 14.5; for *Miscanthus* EF$_{iso}$ = 0 and EF$_{other}$ = 43.2 and 24.8 for unfertilized and fertilized plots, respectively). The results were used to calculate emissions (in µmol per ground area) for the two indicated fractions, considering dynamic leaf area changes.

To get an estimate on potential impacts on air chemistry, we estimated the OH· reactivity of our *Salix* and *Miscanthus* plantations. For this purpose, we calculated the OH· reactivity from all emitted compounds by using the AopWin™ module of the EPI™ software suite (https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface, EPA, USA) (previously used for same calculations by Hakola et al., 2017). OH· reactivity of individual VOCs is indicating how the VOC components are weighted to derive a joint reactivity for all non-isoprene compounds. Importantly, the assumption of a constant VOC mixture and thus a constant OH· reactivity is a major uncertainty (see also Hakola et al., 2017). In addition, we assume that the rate constants that are defined for 25 °C are valid for the whole temperature range. We multiplied the reactivity rate constants with the simulated emissions (differentiated in isoprene and other VOCs as previously presented) to obtain the total OH· reactivity.

3. Results

3.1. Soil N availability, leaf C and N contents as well as $\delta^{13}C$ and $\delta^{15}N$ signatures

Non-fertilized *Salix* plots contained more N$_{min}$ across the three soil layers (0–90 cm) than non-fertilized *Miscanthus* plots (Supplementary Table S1). Fertilization significantly increased the total N$_{min}$ contents of the uppermost (0–30 cm) but not of the deeper (60–90 cm) soil layers of both species. As a consequence of fertilization, leaf N contents and $\delta^{15}N$-signatures significantly increased, but and C/N ratios in both plant species decreased (Supplementary Table S1). The leaf $\delta^{13}C$ values of both species differed strongly, reflecting C$_4$-photosynthesis in *Miscanthus* and C$_3$-photosynthesis in *Salix*. Fertilization did not affect leaf $\delta^{13}C$ values in both species.

3.2. Leaf physiology and biomass characteristics

Regardless of fertilization, *Miscanthus* showed higher net CO$_2$ assimilation rates (P$_N$) and — as expected for a C$_4$-plant — higher intrinsic water use efficiency (iWUE) than *Salix* (Supplementary Fig. S1). Fertilization enhanced P$_N$ of both species, whereas it did not affect leaf stomatal conductance (g$_s$) and iWUE. In contrast, leaf areas as well as above- and below-ground biomass of *Miscanthus* was lower than in *Salix* (Supplementary Table S2). Fertilization significantly enhanced mean shoot height, leaf area per plant, and weight per plant of both species. The increment of leaf area (255 *vs.* 126%) and biomass (250 *vs.* 205%) of *Salix* responded stronger to fertilization than *Miscanthus*.

3.3. VOC emissions and effects of fertilization

Salix emitted about twice as much total VOC per leaf area unit than *Miscanthus*, independent of the treatment (Fig. 1, Table 1). With a share of 65% of total VOCs, isoprene dominated the emissions of non-fertilized *Salix* (EF 67.0 µg C g^{-1} DW h^{-1}) (Fig. 1; Supplementary Table S3). Among the other compounds emitted from *Salix*, 3-hexen-1-ol-acetate was quantitatively most important, followed by 4-(1,1-dimethyleethyl)-cyclohexanone and 2,4-dimethylhexane-1,3-diol. Moreover, several monoterpenes (linalool, *p*-cymene, limonene) and oxygenated compounds (e.g. acetaldehyde, decanal) were emitted. Fertilization caused a significant increase in isoprene emission to 2.27 µg m^{-2} s^{-1} (EF 100.0 µg C g^{-1} DW h^{-1}), enhancing the share of isoprene to ca. 85% of total VOC emissions. Correspondingly, emission rates of four other compounds (*i.e.* 3-hexen-1-ol-acetate, 2(3H)-dihydro-furanone, 2,6,6-trimethyl-2-cyclohexenone, 4-methyl-2-pentanone) decreased due to fertilization (EF 28.7 µg C g^{-1} DW h^{-1} for non-fertilized, 14.5 µg C g^{-1} DW h^{-1} for fertilized sites). However, fertilization did not affect total VOC emission of *Salix* per leaf area unit.

The most important compounds emitted by *Miscanthus* were n-decanal, 1,4-dimethyl-benzene, phenol, hexanal and dihydro-2(3H)-furanone (Supplementary Table S4). Fertilization reduced the emission rates of 2,4-dimethylhexane-1,3-diol, 1,2,3,4-tetramethylbenzene and 7,7-dimethyl-tetracyclo[4.1.0.0(2,4).0(3,3)]heptane and increased the emission of *p*-cymene, limonene, acetaldehyde, and 2,4-dichloro-benzaldehyde. Similar to *Salix*, fertilization did not significantly affect total VOC emission per leaf area (Fig. 1, Table 1).

The higher leaf-level VOC emission of non-fertilized *Salix* compared to non-fertilized *Miscanthus* was compensated at the plantation level by higher leaf area index of *Miscanthus*. Consequently, emission from non-fertilized *Salix* and *Miscanthus*
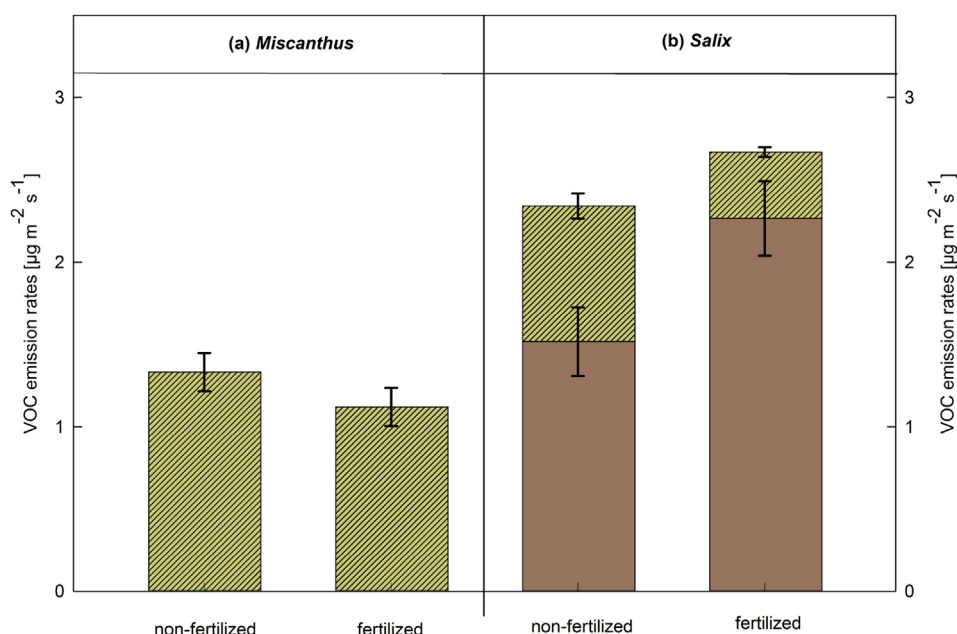
Fig. 1. Effect of fertilization on leaf level VOC emission of *Miscanthus* (a) and *Salix* (b) plants. Means ± SE of total VOC emission rates (stacked columns), isoprene emission (internal brown column), and other VOC except isoprene (internal yellow hatched columns) are shown (n = 5 for non- and fertilized *Salix* and non-fertilized *Miscanthus*; n = 4 for fertilized *Miscanthus*). Emissions were determined under standard conditions (30 °C leaf temperature, 1000 μmol photons m^{-2} s^{-1} PAR). Results of statistical analyses are indicated in Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1

p value indicating statistically significant differences of total VOC emission, isoprene emission and emission of other VOC except isoprene. Unpaired Student's t-tests were applied to test for interspecific (*Miscanthus vs. Salix*) differences at same treatments (non-fertilized, fertilized) and fertilization effects (control *vs.* fertilized) for each species at the leaf level (a) and the plantation level (b). Significant difference are indicated bold.

(a) leaf level	interspecific comparison		fertilization effects	
	non-fertilized	fertilized	*Miscanthus*	*Salix*
total VOC	**0.001**	**<0.001**	0.234	0.257
isoprene	**<0.001**	**<0.001**	1.000	**0.041**
other VOC except isoprene	**0.006**	**<0.001**	0.234	**<0.001**
(b) plantation level	interspecific comparison		fertilization effects	
	non-fertilized	fertilized	*Miscanthus*	*Salix*
total VOC	0.058	**0.001**	0.341	**<0.001**
isoprene	**<0.001**	**<0.001**	1.000	**<0.001**
other VOC except isoprene	**0.008**	**<0.001**	0.341	0.083

Emission data are shown in Figs. 1 and 2.

plantations did not differ on a ground area basis (per ha) (Figs. 1 and 2, Supplementary Table S2). However, fertilization significantly increased (ca. 3-fold) the total VOC emission from *Salix* plantation (170.00 ± 12.92 *vs.* 58.03 ± 4.39 mg ha^{-1} s^{-1}; *p* < 0.001, Fig. 2) because of a much higher leaf area in the fertilized system. Therefore, *Salix* showed two-fold higher VOC emission in response to fertilization than *Miscanthus* (*p* < 0.001, Fig. 2).

Multivariate analysis (*i.e.* PCA) of VOC emission patterns revealed a distinct separation of fertilized and non-fertilized plants of *Miscanthus* and *Salix* (Fig. 3a and b). PC1 explained 45.9% and 93.8% of the total variation in both species, respectively (Fig. 3a and b). The loading plots resulting from PCA indicated that differences in the emission of 3-hexen-1-ol-acetate, 1,2,4-trimethyl-benzene, 2,4-dichloro-benzaldehyde, 1,4-dimethyl-bezene, *p*-cymene and limonene were the main compounds determining the fertilization-caused clustering in *Miscanthus* (Fig. 3c and Supplementary Table S4). Whereas differences in the emission of 3-hexen-1-ol-

acetate, 4-(1,1-dimethylethyl)-cyclohexanone, *p*-cymene, 4-mehyl-2-pentanone, limonene, 1,4-dimethyl-bezene and 1-ethyl-2,3-dimethyl-benzene were responsible for fertilization effects in *Salix* (Fig. 3d and Supplementary Table S3).

3.4. C sequestration by biomass accumulation

Carbon sequestration for a whole lifecycle of 16 years was calculated by modelling, which was adjusted to the measured data in 2010 (Table 2). In the first four years, gross primary production (GPP) was considerably smaller in *Miscanthus* than in *Salix*. In the modelling exercise *Salix* reached relatively strong C sequestration already after the first year, which was due to the previous clear cutting of all stems that provoked full re-sprouting. Consequently, the first four years in the *Salix* plantations were not much different from the following rotation periods. Fertilization caused further increase of GPP in both rotations (16.3–23.6 tC ha^{-1} a^{-1} in years 1–4 and 15.2 to 23.1 tC ha^{-1} a^{-1} in years 5–16).

In contrast to *Salix*, GPP of non-fertilized *Miscanthus* plantations were 2.7-fold lower in years 1–4 than in the subsequent years 5–16. Fertilization caused strongly increased GPP in years 1–4 and years 5–16 (Table 2). Because of the less developed rooting system, belowground respiration in *Miscanthus* was considerably lower than in *Salix*, particularly in years 1–4. In contrast, aboveground and total ecosystem (R_{eco}) respiration was of similar magnitude as the *Salix* plantations irrespective of the fertilization regime. Net primary production (NPP) of non-fertilized *Salix* plantations amounted to 62% of the fertilized plantation. Fertilization had a much stronger effect on *Miscanthus* as NPP of fertilized plantations showed almost 2.5-times higher NPP than non-fertilized plantations.

3.5. Simulated annual VOC emissions and resulting OH· reactivity

Estimating annual VOC emission from both plantation systems required a realistic representation of the seasonal leaf biomass and
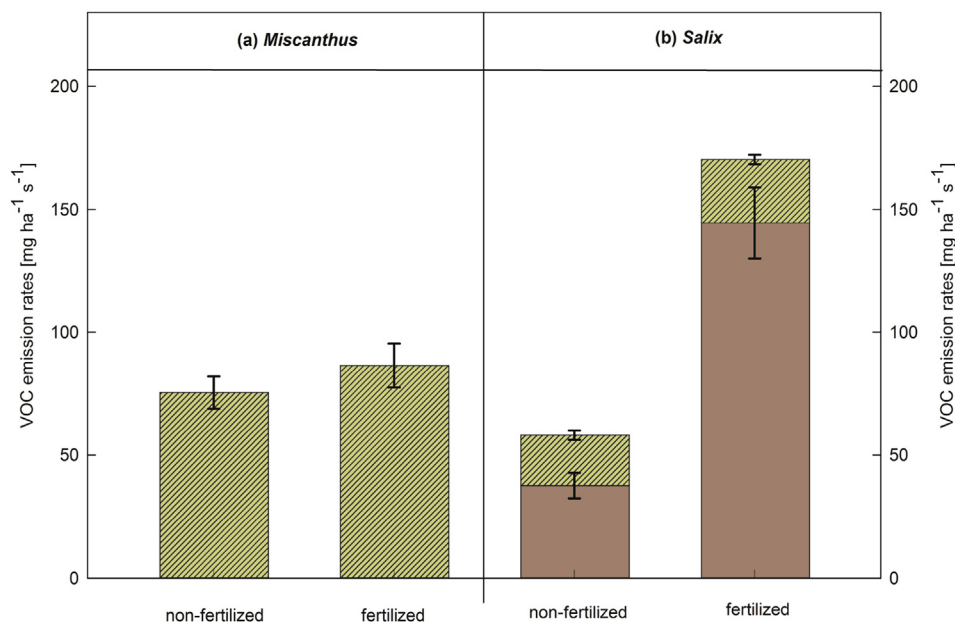
Fig. 2. Effect of fertilization on plantation level VOC emissions of *Miscanthus* (a) and *Salix* (b). Means ± SE of total VOC emission rates (stacked columns), isoprene emission (internal brown column), and other VOC except isoprene (internal yellow hatched columns) are shown (n = 5 for non- and fertilized *Salix* and non-fertilized *Miscanthus*; n = 4 for fertilized *Miscanthus*). Results of statistical analyses are indicated in Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

plant development. Herein, this was accomplished by calibrating the maximum leaf biomass for the different fertilization regimes to the measurements. Phenology and N uptake, which also affect foliage dynamics, were calculated according to an initial previous parameterization and site initialization with data from the year before the experiment started (*i.e.* in 2009) (see Fig. 4). Using the determined EF from June 2010 as input parameters for modelling, we estimated for *Salix* total annual isoprene emissions of 95 and 196 mmol C ha^{-1} year^{-1} depending on the fertilization regime. Annual emissions of other VOCs amounted to 60 and 75 mmol C ha^{-1} a^{-1} (non-fertilized and fertilized systems, respectively). For *Miscanthus* VOC emissions amounted to 154 and 123 mmol C ha^{-1} year^{-1} in non-fertilized and fertilized systems (Table 3). Thus, the simulations show that despite the decrease of EF for other VOCs than isoprene in both species, the emissions at the fertilized plots are still in the same order of magnitude due to the increased amount of foliage.

Interestingly, the output of other VOCs (on a mole basis) is considerably larger than can be expected from the comparison of emission factors (e.g. EF$_{iso}$ for unfertilized *Salix* is about double that of EF$_{other}$ but the isoprene emission is only 1.5 the emission of other VOCs). This is because the isoprene EF depends on light as well as previous cumulative weather conditions, which both diminish the potential EF particularly during spring and autumn.

The VOC emission rates were used to calculate OH$^{\cdot}$ reactivity for both plantation systems over a whole year (Fig. 4 c, f). Importantly, the difference observed for VOC emissions between *Miscanthus* and *Salix* was strongly enhanced regarding OH$^{\cdot}$ reactivity. This was mainly due to the emission of isoprene from *Salix* plantations as isoprene exerts a much stronger OH$^{\cdot}$ reactivity than the oxygenated compounds released by *Miscanthus* (see Supplementary Table S5). Roughly, *Salix* systems showed ca. 8-times higher OH$^{\cdot}$ reactivity over the season than *Miscanthus* plantations.

4. Discussion

4.1. The two cropping systems clearly differ in VOC emissions

Our results revealed clear differences in VOC emissions from leaves of *Miscanthus* and *Salix*. In *Salix* the overall standard emission rates were ca. 1.5 times (non-fertilized plants) and ca. 2.5 times (fertilized plants) higher than in *Miscanthus* (Fig. 1). In accordance with previous reports (e.g. Copeland et al., 2012; Morrison et al., 2016), the emission pattern of *Salix* was dominated by isoprene, which contributed about 65% and 85% to the total VOC emissions in non-fertilized and fertilized plants, respectively. Salicaceae, in particular willow and poplar belong to the strongest emitters of isoprene (Rosenkranz et al., 2015). Isoprene emission rates in our study amounted to 20–30 nmol m^{-2} s^{-1} (similar to 75–113 μg g^{-1} DW h^{-1}) with EFs of 67 and 100 μg C g^{-1} DW h^{-1} of non-fertilized and fertilized plants, respectively. In comparison, EFs for isoprene emission from willow have been reported to be highly variable ranging between 0.1 and 115 μg g^{-1} DW h^{-1} (Morrison et al., 2016) while the EFs for isoprene currently applied in models for *Salix* range between 37 and 98 μg g^{-1} DW h^{-1} (Steinbrecher et al., 1999; Klinger et al., 2002; Karl et al., 2009). Such high variability in isoprene emission of *Salix* can be explained by the species and genotype considered (Eller et al., 2012), but also by the seasonality of isoprene emission. For example, Hakola et al. (1998) studying isoprene emissions under standardized conditions from *Salix phylicifolia* leaves observed very low emissions 2–3 weeks after leafing in May. Thereafter, the emission rates increased steadily during the vegetation period, reaching a maximum from the end of August until the end of September. This effect is at least partly reflected in the model, assuming a parallel development of emission potential and leaf phenology as well as a dependency on the temperature regime of the previous ten days.
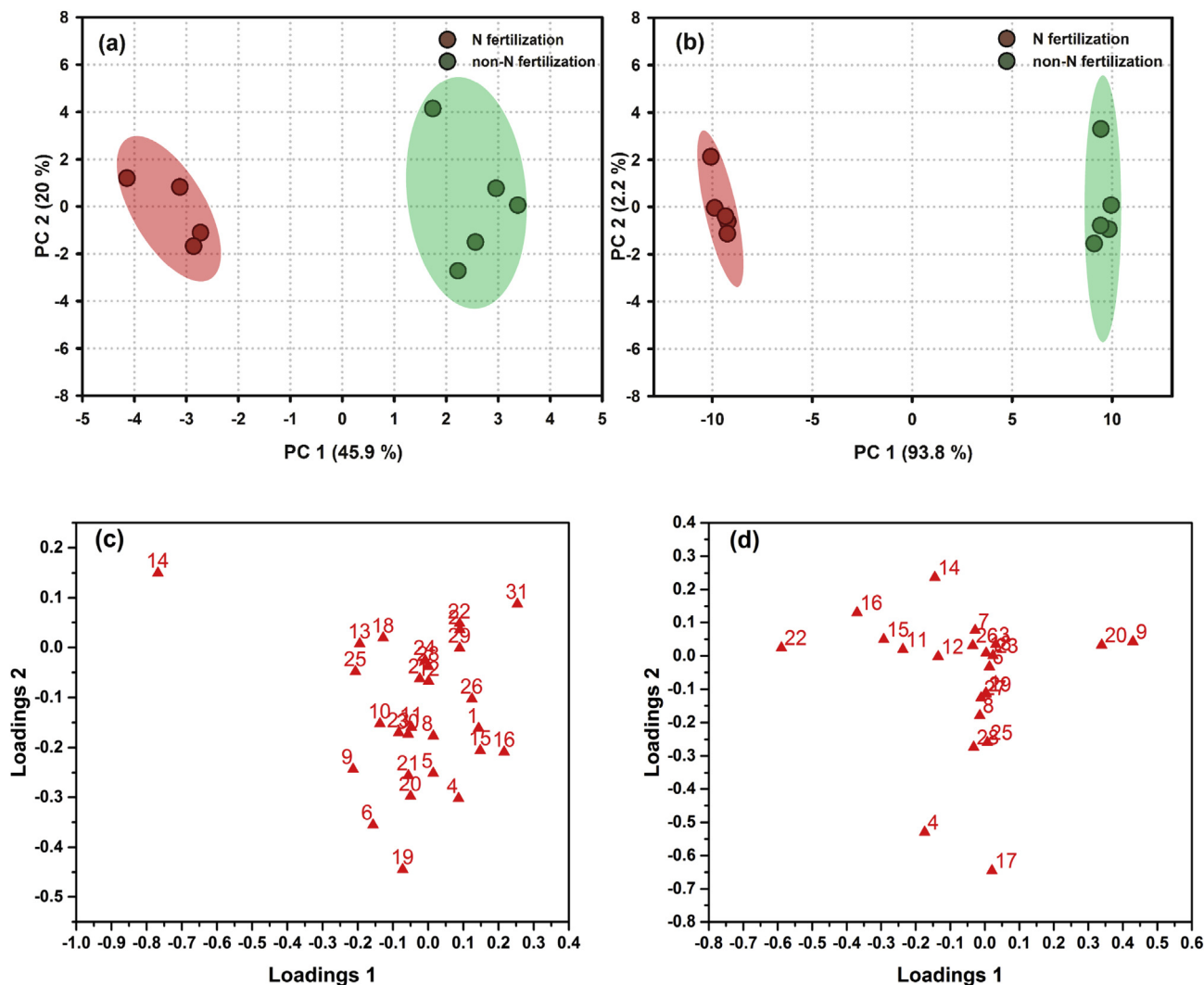
Fig. 3. Principal component analysis (PCA) (a, b) and PCA loadings plots (c, d) of VOC emission patterns of non-fertilized (green) and fertilized (red) *Miscanthus* (a, c) and *Salix* (b, d) plants. Ellipses indicate the 95% confidence range. Numbers in loadings plots (c, d) indicate the VOC compounds listed in Supplementary Tables S3 and S4, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Annual plant C balances from *Miscanthus* and *Salix* plantations with two N-fertilization rates (F = fertilized, NF = non-fertilized) simulated for an entire plantation life cycle of 16 years. Total fluxes are representing weighted means over the entire period.

		GPP [tC ha^{-1} a^{-1}]			R_{eco} [tC ha^{-1} a^{-1}]						NPP [tC ha^{-1} a^{-1}]
		year 1–4	year 5–16	total	below ground		above ground		total		total
					year 1–4	year 5–16	year 1–4	year 5–16			
Salix	NF	16.3	15.2	15.5	3.9	4.0	2.8	1.6	5.9		9.6
	F	23.6	23.1	23.3	6.0	7.0	1.1	1.0	7.8		15.5
Miscanthus	NF	6.0	19.0	15.8	1.8	3.5	1.6	5.5	7.6		8.2
	F	16.2	34.4	29.9	2.1	4.4	2.8	7.1	9.9		20.0

GPP: gross primary production; R_{eco}: ecosystem respiration; NPP: net primary production.

In *Salix*, oxygenated compounds (e.g. 3-hexen-1-ol acetate, 4-(1,1-dimethylethyl)-cyclohexanone, hexanal, acetaldehyde) as well as some monoterpenes (δ-3-carene, linalool, *p*-cymene, limonene) were also emitted, but they were of minor quantitative importance at the leaf level. The monoterpene emission rates from *Salix* varied from 2-44 ng m^{-2} s^{-1} (equivalent to 0.1–2.2 µg g^{-1} DW h^{-1}). These rates are in the same range of published data on monoterpene emission of *Salix* (0–1.2 µg g^{-1} DW h^{-1}, Evans et al., 1982; Helmig

et al., 1999; Owen et al., 2003; Karl et al., 2009). Similar to isoprene, seasonal patterns of monoterpene emission rates can be a reason for the observed strong variations. However, *Salix* seems to emit monoterpenes at considerably higher rates in spring directly after leaf development and emissions decrease thereafter (Hakola et al., 1998), which indicates a possible ontogenetic mechanism that is not yet possible to represent in emission models. Release of acetaldehyde, hexanal, heptanol, decanal, hexenol acetate and
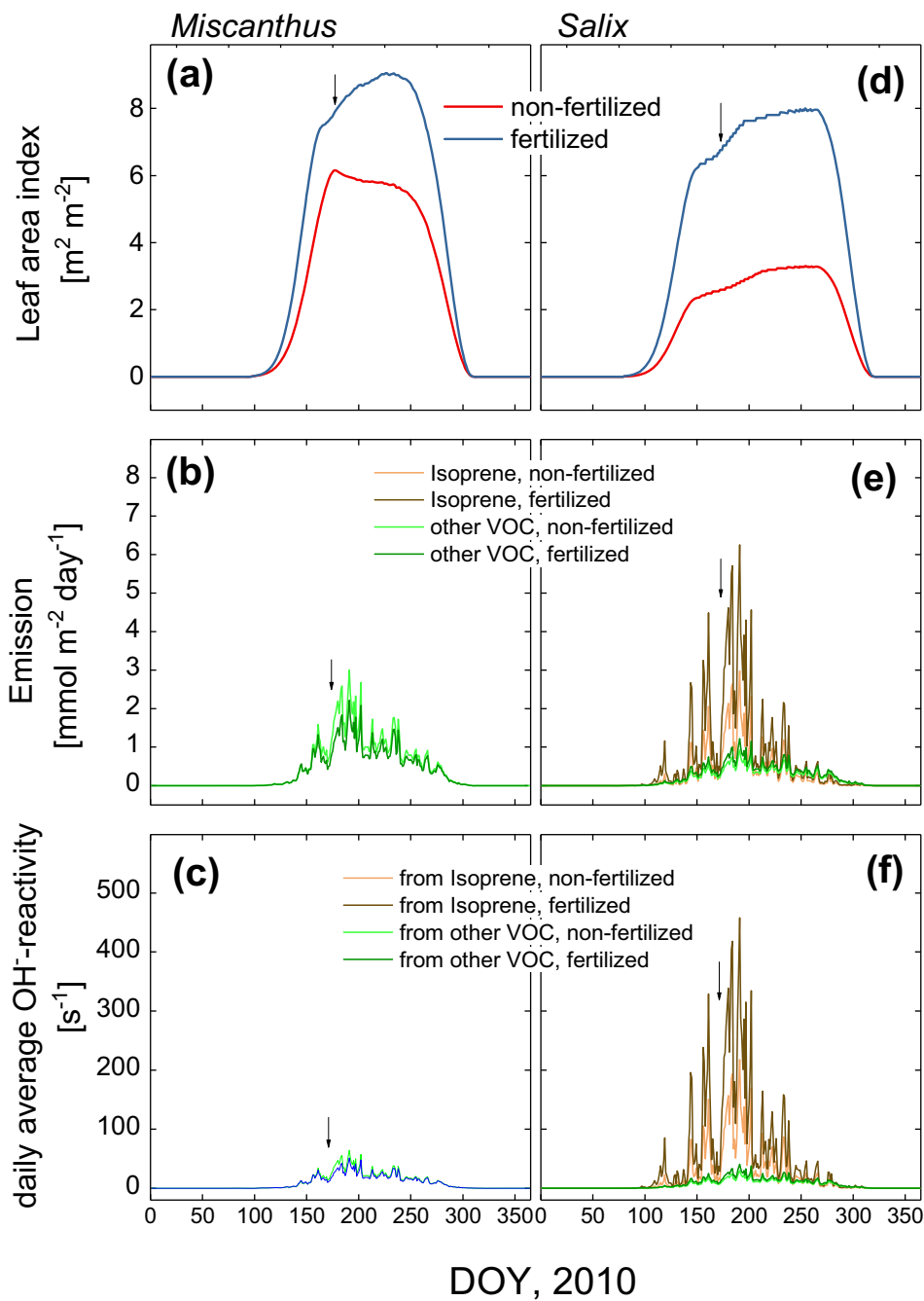
Fig. 4. Simulated leaf area index (a, d), VOC emission rates differentiated into isoprene and other VOCs as explained in the text (b, e), and daily average OH· reactivity (c, f) from *Miscanthus* (a, b, c) and *Salix* (d, e, f) plantations under fertilized and non-fertilized conditions for weather conditions of the year 2010. The arrows indicate the period where EFs were experimentally determined. DOY: date of the year.

Table 3
Annual emission of VOCs from *Miscanthus* and *Salix* plantations as affected by fertilization. Emissions were simulated with weather data of 2010 and emission factors determined during a field campaign in June 2010.

	Miscanthus		*Salix*	
	non-fertilized	fertilized	non-fertilized	fertilized
Isoprene [mmol m^{-2} (ground) year^{-1}]	0	0	95	196
Other VOCs [mmol m^{-2} (ground) year^{-1}]	154	123	60	75

others as observed for *Salix* herein has also been demonstrated earlier (Geron et al., 2000). These compounds are commonly reported as typical oxygenated VOCs released from the foliage of many other plant species with very similar emission rates than in our study (Owen et al., 1997; Kreuzwieser et al., 2001; Wildt et al., 2003; Seco et al., 2007; Jardine et al., 2010).

The emission pattern observed for *Miscanthus* in the present work, significantly differed from the pattern seen in *Salix* (Supplementary Tables S3 and S4). Similar to other monocotyledons (*Miscanthus*: König et al., 1995; Copeland et al., 2012; Morrison et al., 2016; *Miscanthus*, switchgrass, different prairie grasses: Miresmailli et al., 2013; switchgrass: Eller et al., 2011; maize and switchgrass: Graus et al., 2013; maize: Das et al., 2003; Leppik et al., 2014; Wiß et al., 2017), *Miscanthus* did not emit isoprene or its release was below the limit of detection. Instead, we observed the release of several carbonyls, aromatics, alcohols and a few monoterpenes (Supplementary Table S4). None of these compounds dominated the emission pattern of *Miscanthus*. The most abundant VOCs released by *Miscanthus* were the aldehydes decanal and hexanal, and the aromatics dimethyl benzene and phenol. Release of these compounds was also observed in a variety of other plant species with emission rates in the same range as found in the present study on *Miscanthus* (e.g. hexanal: $0.009-0.036\,\mu g\,g^{-1}\,h^{-1}$ from leaves of various herbaceous and conifer species, see Wildt et al., 2003; Filella et al., 2007; decanal: $0.01-20\,\mu g\,g^{-1}\,h^{-1}$ from various plant species, see Owen et al., 1997; phenol: $0.13-2.48\,\mu g\,g^{-1}\,h^{-1}$, see Helmig et al., 1999; Penuelas and Llusia, 2001; xylene: EF $10.7-26\,\mu g\,m^{-2}\,h^{-1}$, see Wiß et al., 2017). The release of *p*-xylene was qualitatively demonstrated also from grassland vegetation (Fukui and Doskey, 2000) and a stone pine forest site (Song et al., 2011). In contrast, dihydro-furanone emission from leaves was so far not described, but this furan derivative was abundant, for example, in barley roots (Gfeller et al., 2013). Monoterpene (limonene, linalool, *p*-cymene) emission from *Miscanthus* in the present study amounted to ca. $14-43\,ng\,m^{-2}\,s^{-1}$ (*i.e.* $0.69-2.36\,\mu g\,g^{-1}$ DW h^{-1}), which was in the lower range of reported monoterpene emissions of *Miscanthus* ($0-802\,\mu g\,g^{-1}$ DW h^{-1}; Morrison et al., 2016), but very similar to the range of monoterpene release of maize ($26-58\,ng\,m^{-2}\,s^{-1}$; Wiß et al., 2017). However, overall the emissions of VOC from *Miscanthus* were in the upper range of previously reported emission rates (Supplementary Table S4) (Copeland et al., 2012; Miresmailli et al., 2013; Morrison et al., 2016). Interestingly, *Miscanthus* emitted several different benzenoids (e.g. 1,4-dimethyl-benzene, 1,2,3,4-tetramethylbenzene, benzoic acid, propyl-benzene, 1,2,4-trimethyl-benzene, 1-methyl-3-(1-methylethyl)-benzene, 4-methoxy-benzaldehyde, 1-ethyl-2,3-dimethyl-benzene) into the atmosphere (Supplementary Table S4). Such compounds and other aromatics including phenols (White et al., 2009) have been recognized to be released from different plant species into the environment and are discussed to significantly contribute to the formation of secondary organic aerosols (SOA) (Misztal et al., 2015). The biosynthesis and emission of several benzenoids seems to be stimulated by abiotic (e.g. heat) and biotic (e.g. herbivore attack) stresses. Interestingly, the emission rates observed in our study were very similar to the emission rates of stressed *Populus balsamifera*, whereas other species (*Pinus sylvestris, Picea abies, Betula, Populus tremula × tremuloides*) emitted these compounds at lower rates. The high hexanal emission rates support the view that the *Miscanthus* plants were stressed to some degree. However, because we did not recognize any visible sign of biotic stress, we assume that the strong benzenoid emission observed in our study with *Miscanthus* reflects constitutive emissions and that were not induced by any stress. It is speculative if herbivore attack or abiotic stresses would cause induction of further benzenoid biosynthesis leading to even enhanced emission of benzenoids (Misztal et al., 2015).

4.2. Effects of N on emission and photosynthesis

Main aim of the present study was to quantify the influence of N fertilization on VOC emissions from two bioenergy plantation systems. At leaf level, basal isoprene emission potentials (EFs) in *Salix* were increased by about 50%, in agreement with our hypothesis (ii), while the emissions of other VOCs were only about half as high as from non-fertilized plots. As it is generally known that N fertilization negatively correlates to the formation of phenolic compounds (Bryant et al., 1983), it might be that the observed reduced emission of some volatile benzenoids (e.g. 1,4-dimethyl-benzene, 1,2,3,4-tetramethylbenzene, 1,2,4-trimethyl-benzene) from *Miscanthus* (Supplementary Table S4) results from such plant internal shifts. This does not exclude occasional higher emission potentials of single compounds such as the oxygenated monoterpene linalool in *Salix* (Supplementary Table S3). The response of the emission of individual VOC to N fertilization therefore seems to be compound specific and probably related to the different biosynthetic routes and the environmental drivers triggering them.

Similar stimulating (ocimene, hexanal, DMNT) and decreasing (*α*-pinene, *β*-pinene) effects of N fertilization on the emission of specific VOCs were observed by Carriero et al. (2016) in *Betula pendula*. The enhanced emission of terpenoids in response to fertilization as reviewed by Ormeño and Fernandez (2012), was supported herein for limonene and *p*-cymene in *Miscanthus*, but was not found for linalool in the same species. In *Salix*, on the other hand, linalool and isoprene emission increased due to N fertilization but not the release of other terpenoids (*p*-cymene and limonene). Apparently, N fertilization seems to enhance the abundance of terpenes in leaves of several woody species (Ormeño et al., 2008), which fits well with the observed emissions of these compounds. In accordance with our work and hypothesis (ii), isoprene emission (Monson et al., 1994; Litvak et al., 1996) increased at higher soil N supply, suggesting that higher leaf N content contributes to enhanced enzymatic activity involved in terpene biosynthesis.

Nitrogen fertilization influenced leaf physiology of both species in several ways. The better N availability in the soil significantly caused higher leaf N contents in *Salix* and *Miscanthus*, as also seen in many other N fertilization experiments with *Miscanthus* and other plant species (Lerdau et al., 1995; Pääkkönen and Holopainen, 1995; Wang et al., 2012; Carriero et al., 2016). We assume that the increased leaf N content at least partially reflects higher ribulose bisphosphate carboxylase (Rubisco) protein contents and enzyme activities, which would explain the significantly enhanced net CO_2 assimilation rates (P_N) in both plant species upon N fertilization (Supplementary Fig. S1). Comparable effects of N fertilization on net CO_2 assimilation were observed in many other plant species (e.g. Douglas fir and *Salix*; Brix, 1981; Evans, 1989; Vapaavuori and Vuorinen, 1989; Mitchell and Hinckley, 1993).

As expected, iWUE of *Miscanthus* reflected the more efficient water use of this C_4 plant as compared to the C_3 plant *Salix* (McKendry, 2002). Although other studies reported that N fertilization has synergistic interactions with reduced water regimes on the plant growth (Cosentino et al., 2007; Yin et al., 2009), we could not verify this effect in the present study under common water conditions. In fact, increased P_N but unchanged stomatal conductance indicates that iWUE (i.e. A/g_s) was not affected in both investigated species by N application. Thus, N fertilization could increase plant growth based on higher rates of carbon fixation (P_N) without enhanced water loss (Hillerdal-Hagströmer et al., 1982).

The leaf $\delta^{13}C$ signatures, integrating gas exchange signals over longer periods of time (some weeks to months, Hartman and Danin, 2010; Brüggemann et al., 2011), give further insight into plant water use (Roussel et al., 2009; Brüggemann et al., 2011; Saugier et al., 2012). In the present study, we did not observe any fertilization effects on current $\delta^{13}C$ signatures and iWUE in both species, indicating that plant iWUE is not affected by fertilization in the long-term. Similar effects of improved N supply on leaf gas exchange were observed with *Pinus sylvestris*, *Pinus radiata* and *Pseudotsuga menziesii* (Brix, 1981, 1983; Hillerdal-Hagströmer et al., 1982; Squire et al., 1987). However, these effects might change under drought conditions that did not occur during our measuring campaign. Nevertheless, fertilized plants may have larger stress than non-fertilized ones under dry conditions (Cosentino et al., 2007; Yin et al., 2009).

4.3. From leaf level to plantation level

To evaluate the C balance and the VOC emission from the two cropping systems, up-scaling of leaf-level data to the plantation level was performed by using an evaluated model for estimating leaf area development under fertilized and non-fertilized conditions. On the basis of our measured biomass parameters, the model showed that N fertilization clearly stimulated plant growth (Supplementary Tables S2 and S6), which agrees well with earlier work (Taylor et al., 1993; Gastal and Lemaire, 2002; Wang et al., 2012; Carriero et al., 2016). More available N enhances photosynthesis efficiency as well as the formation of new leaves and, consequently, increases the plants' leaf area (Meier and Leuschner, 2008). Hence, the observed increased growth of fertilized plants was due to a combined stimulating effect on leaf level photosynthesis and on leaf area (e.g. McDonald et al., 1986; Dreccer et al., 2000). The finding of Clifton-Brown and Jones (1997) suggesting that biomass production of *Miscanthus* is more controlled by leaf extension than by increased leaf level photosynthesis, is therefore not fully supported by the present and other observations (Wang et al., 2012).

Besides effects on the shoot, N fertilization can also influence belowground C allocation (Heinsoo et al., 2009). Although fine root dynamics was not studied in our field experiment, and species-specific responses are highly variable (Cunniff et al., 2015), a higher belowground investment would lead to additional (autotrophic) respiration, which would compensate for higher (heterotrophic) respiration due to decomposition in nutrient rich soils, as observed at the same study site by Gauder et al. (2012).

Based on the modelling results, total annual C sequestration (NPP) can be of comparable magnitude in *Salix* and *Miscanthus* plantations. However, this depends highly on nutrient availability because *Salix* seems to be less sensitive to N supply, whereas *Miscanthus* is able to sequester more C if fertilized. Comparison with literature results is difficult since in most cases only yield or aboveground productivity is provided. However, assuming that the fraction of belowground productivity is about one third of aboveground levels (Rytter, 2001; Gauder et al., 2016), our results are well in the range of reported *Miscanthus* productivities (e.g. Heaton et al., 2010; Iqbal et al., 2015) and similar or somewhat higher than assumed for *Salix* SRC plantations (Rytter, 2012; Wang et al., 2015).

Apart from isoprene being the overall dominating compound in *Salix*, we estimated that the emission of terpenoids and other VOC were only marginally influenced (a bit higher in *Salix* and a bit lower in *Miscanthus*) by the level of N fertilization we applied herein. However, EF of isoprene emissions in the *Salix* system increased due to fertilization and, therefore, total emissions were approximately doubled. Increasing leaf area accounted for approximately 80% of this increase. As already mentioned, emission rates of other VOC were relatively high for *Salix* as well as for *Miscanthus* although we did not observe strong infestation with herbivorous insects or other biotic stressors. Moreover, the clear positive dependency between potential isoprene emission and N supply of *Salix* is very indicative, pointing towards a better supply of precursor availability for terpenoid production (Monson, 2013).

It should also be mentioned that some uncertainty is connected to the standard parameters used in the model regarding the VOC emission estimates. For example, Niinemets et al. (2013) have shown that light and temperature dependency curves described by the Guenther algorithm (Guenther et al., 1995) may vary from the standard assumption for particular species and environmental conditions. It cannot be excluded that the EF that were determined during the field campaign are also varying due to influences not considered in the model. In particular, we do not know if the nutritional influence is actually constant over the whole vegetation period (Lerdau et al., 1995). Other environmental stress effects and ontogenetic developments might also affect EF rates. For example, recent work on maize highlighted that in particular flowering periods might affect the composition and amount of VOC emissions (Wiß et al., 2017). Moreover, insect infestation and abiotic stress might influence plantation VOC emissions (Kessler and Baldwin, 2001; Holopainen and Gershenzon, 2010; Niinemets et al., 2013; Yli-Pirilä et al., 2016). Unfortunately, models cannot yet describe these influences and more or continuous emission measurements that can be used for further model improvements or at least to an empirical consideration are seldom available. It is, however, likely that many of these effects would affect fertilized as well as unfertilized sites to similar degrees, thus, having only minor impact on the main results of this study.

4.4. Significance of VOC emissions from the two cropping systems

Our simulation approach clearly indicated that the *Salix* plantation caused a much (8-times) higher OH· reactivity compared to *Miscanthus*. This was, on the one hand caused by different VOC emission rates of the two plant species, on the other hand by the strong isoprene emissions from *Salix* (Fig. 4). Despite the high uncertainty (Hunter et al., 2017 assume a 30 percent uncertainty for the rate constants alone), the results demonstrate that isoprene is dominating the OH· reactivity in *Salix* even more strongly than can be assumed from its share of overall emission. In addition, the higher reactivity in fertilized *Miscanthus* sites partly compensates for the lower VOC emissions so that the OH· reactivity of fertilized and unfertilized sites is more similar than their emission amounts.

Since significant isoprene emission could affect local and regional air quality by influencing tropospheric ozone production and SOA formation (Copeland et al., 2012; Ying et al., 2015; Venkanna et al., 2016), it has been argued that an increasing abundance of isoprene emitters (e.g. *Salix* in the present study) could negatively affect local air quality (Ashworth et al., 2012). Therefore, similar to conventional crops, the non-isoprene emitter *Miscanthus* might have a lower influence on air quality than *Salix*. However, we did not assess VOC emissions during the whole vegetation period and high transient emissions, for example of sesquiterpenes during the time of flowering (Wiß et al., 2017) or stress-induced emissions from *Miscanthus* might change this picture. Moreover, recent research has shown that the emission of monoterpenes and other compounds with higher molecular weight can stimulate the formation of biogenic secondary aerosols (SOA) (Xu et al., 2015; Dal Maso et al., 2016). Therefore, a high abundance of plants emitting such substances likely affects the regional radiation regime either directly or indirectly by stimulating cloud formation. Indeed, the emissions from *Miscanthus* found in this study

are considerably higher than currently assumed in regional and global models.

For an overall conclusion on the environmental impact of *Salix* and *Miscanthus* bioenergy plantations not only biomass production and VOC emission, but also nitrate leaching and the release of the GHG CH_4 and N_2O have to be considered. With regard to GHG emission, Gauder et al. (2012) demonstrated at the same *Salix* and *Miscanthus* field sites that release of these gases is negligible and that under non-fertilized conditions rather an uptake than an emission took place. In order to judge the benefits of biomass production for different bioenergy crops, VOC emissions can be related to productivity. If normalized to OH· reactivity, non-fertilized *Salix* plantations were responsible for 925 s^{-1} per toC, which increased to 1087 s^{-1} per toC in the fertilized system. In contrast, *Miscanthus* only formed 404 and 142 s^{-1} per toC in non-fertilized and fertilized plantations, respectively. Taken together, *Miscanthus* plantations seem provide some advantages over *Salix* SRC regarding ecological impact, particularly if related to productivity. Nevertheless, other aspects such as different management practices have to be considered for a complete LCA.

Acknowledgement

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.02.034.

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