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Ontogenetic, diurnal, and environmental impacts on VOC emission from sugarcane

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ABSTRACT

Sugarcane (*Saccharum* spp. hybrid) is a key crop for bioenergy production due to its high productivity in tropical and subtropical climates. Despite this economic importance, there is currently no information available on the emission of volatile organic compounds (VOCs) during the growth phase of this crop. This is despite the fact that the sustainability of sugarcane cultivation has been questioned due to the associated land-use changes and possible atmospheric pollution by VOCs. The present study investigated the VOC emissions from sugarcane and their dependence on ontogenetic, diurnal, seasonal and environmental factors. By GC–MS and PTR-MS analysis, the emission of 40 different VOCs from sugarcane leaves was recorded based on their molecular weight that were divided into seven chemical groups (*i.e.,* alkanes, alkenes, aromatics, aldehydes, alcohols, ketones and terpenoids). In addition, complementary PTR-MS analysis showed strong emission of methanol, acetaldehyde and ethanol and minor release of monoterpenes, fatty acid derivatives (*i.e.,* LOX products) and a compound with *m/z* 69 (which was not validated as isoprene). Compared to other bioenergy crops, *e.g.,* maize, *Salix, Miscanthus* and poplar/aspen, terpenoid emissions play a quantitatively smaller role, indicating that sugarcane is a low impact species in terms of air chemistry. The VOC emissions from sugarcane leaves vary with plant developmental stages, during the day and between the seasons and are dependent on light intensity and temperature. Thus, our results could provide a valuable basis for future modelling efforts to upscale VOC emissions from sugarcane cultivation in different climatic zones.

1. Introduction

Bioenergy from plant biomass accounts for about 70 % of renewable energy production and contributes about 20 % to global primary energy consumption. This has made it the most important renewable energy source worldwide for decades (IEA, 2014, Licence: CC BY, , 2014; Kaltschmitt, 2011; Long et al., 2013; REN21, 2016). Increased cultivation of fast-growing woody and grass-like plant species is considered a promising approach to increase renewable energy production and has been proposed for different regions of the world (Ericsson et al., 2009; Gauder et al., 2012; Schweier et al., 2017). In central Europe, fast-growing trees such as willows (*Salix* spp.) and poplars/aspen (*Populus* spp.) are often recommended for high-yield bioenergy plantations (Gauder et al., 2012; Boehmel et al., 2008), but also perennial grasses with high growth potential (Boehmel et al., 2008), such as the grass of *Miscanthus* spp., belonging to the group of C4 plants. This group of plants is considered to constitute one of the most efficient CO_2 sinks and most productive biomass producers on the planet, often introduced for this purpose in temperate regions (Gauder et al., 2012; Lewandowski et al., 2000; Heaton et al., 2010). In the tropical and subtropical climates of

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South and North America and Australia, sugarcane (*Saccharum* spp. hybrids) is the most important crop. It is a perennial C4 grass of the *Poaceae* family with high biomass production and is mainly used for bioenergy production. With an area of ca. 26.8 million hectares (Mha) in more than 100 countries worldwide, sugarcane is a major crop (Fao, 2022). In Brazil and the southern states of the USA, it covers 24 million hectares and produces 1.6 billion tons of biomass annually as the largest contributor to global biofuel production (Somerville et al., 2010). For this reason, sugarcane ethanol has been highlighted for its environmental benefits. Thus, it is considered an effective option for reducing anthropogenic greenhouse gas (GHG) emissions into the atmosphere (energy balance: 9.1; GHG savings: 85 % and fuel yield: 6900 L ha^{-1}) compared to other crop-based biofuels such as maize, wheat, sugar beet or sorghum (Goldemberg and Guardabassi, 2010; Muñoz et al., 2014; Jaiswal et al., 2017; Bordonal et al., 2018).

Although sugarcane ethanol is considered the most suitable biofuel from an energy conversion point of view, its environmental impact, and sustainability, as well as the impacts of biofuel production on human health, remains controversial (Lapola et al., 2010; Miller, 2010; Robinson et al., 2011). Sugarcane is the only crop that is burned before harvest (Sevimoglu and Rogge, 2016) and sugarcane residues are also burned after harvesting. Both processes result in the release of many pollutants into the atmosphere (Neto et al., 2011). Among the climate-damaging substances that are released into the atmosphere when sugar cane is burned, black carbon and methane are considered short-lived climate pollutants (SLCPs). Black carbon is associated with other substances produced during the combustion of sugarcane biomass, including organic compounds, particulate matter (PM), volatile organic compounds (VOCs) and hazardous polycyclic aromatic hydrocarbons (PAHs). Compared to the global crop area of approximately 26.8 million ha (Fao, 2022), these compounds could contribute to global climate change and regional climate variability (Kaufman et al., 2002; Ramanathan and Carmichael, 2008), with severe implications for human health (Cançado et al., 2006; Chen et al., 2017). A recent assessment of the mutagenicity of particles from sugarcane combustion has demonstrated that PAHs and nitro-PAHs can contribute significantly to DNA damage (De Oliveira Alves et al., 2014; De Oliveira Galvão et al., 2018). Epidemiological studies have shown that emissions from sugarcane burning are associated with an increased risk of hospital admissions for respiratory diseases and hypertension (Cançado et al., 2006; Uriarte et al., 2009). For example, the burning of straw in the fields to produce sugarcane ethanol is a common practice and is the main source of particulate matter in certain areas of Brazil (Scovronick and Wilkinson, 2014; Scovronick, 2016). This practice causes significant respiratory illnesses such as asthma and pneumonia among field workers and the local population, but is often ignored in numerous life cycle assessment studies (Jeswani et al., 2020).

Recently, the emission of biogenic VOCs by sugarcane during its growth and cultivation have received considerable attentions (Ashworth et al., 2013; Graus et al., 2013), because it constitutes one of the major sources of hazardous air pollutants (HAPs) (Hall et al., 2012; Mugica-Álvarez et al., 2018). However, there is still a lack of data on VOC emissions from sugarcane, particularly from the leaves of sugarcane plants during their growth and development. The emitted VOCs can have a significant impact on regional air chemistry and quality, which in turn affects human health. Depending on their reactivity with hydroxyl radicals (OH), they contribute to the formation of the pollutant and tropospheric GHG ozone (Atkinson and Arey, 2003), but also to the formation of secondary aerosols (SOAs), which counteract global warming (Claeys et al., 2004). VOCs also have an indirect effect on global warming by attenuating atmospheric (OH) concentrations and thereby increasing the half-life of atmospheric CH_4 (Pike and Young, 2009). Although thousands of different VOCs are emitted to the atmosphere by vegetation, in many cases the formation of VOCs can be traced back to a few synthetic pathways that branch off from primary metabolism.

The molecular structure of VOCs emitted by plants allows four main groups to be distinguished: terpenoids, fatty acid derivatives (LOX products), aromatic VOCs and oxygenated compounds with C1-C2 carbon chains (OVOCs) (Gouinguené et al., 2001). Despite the regionally dominant cultivation of sugarcane during harvest and the significant impact of industrialized processes on area-wide GHG emissions (Jeswani et al., 2020; Chami et al., 2020), as well as on regional air chemistry, quality and human health (Jeswani et al., 2020; Chami et al., 2020); there is a lack of knowledge in literatures about VOC emissions of sugarcane, particularly for their source strength and emission patterns during growth over the growing season.

In general, the VOC emissions from plants are primarily influenced by the phenotype and phylogenetic plant origin. This is due to the genetic characteristics of plants, that result in species-specific morphological and physiological properties (Köllner et al., 2004; Gouinguené et al., 2001; Staudt et al., 2010). These characteristics, including stomatal function, storage tissue formation, enzyme activity, shape/size of emitting tissues and surfaces, largely determine the specificity of VOC emissions (Llusia et al., 2014). However, morphological and physiological changes often occur during plant development, including defense and protection mechanisms, which may influence VOC emission at the metabolic and/or physiological level (Loreto and Schnitzler, 2010). Since the leaf is the largest VOC-emitting tissue, it is particularly important to know the source strength and patterns of VOC emissions as a function of plant development up to senescence. The formation and emission of many VOCs is dependent on light and temperature, resulting in pronounced diurnal and seasonal variations (*e.g.,* 46–47). To date, no information about such dynamics is available for sugarcane.

In the present study, we characterized VOC emissions from sugarcane leaves and quantified their dependence on ontogenetic, diurnal and environmental factors. In addition, we estimated the impact of sugarcane VOC emissions on atmospheric chemistry by modelling the hydroxyl (OH) reactivities of the most frequently emitted compounds. We hypothesized that (i) OVOCs and lipoxygenase (LOX) products are the dominant compounds among the VOCs emitted from sugarcane, while terpenoids contribute only small to moderate amounts to the total emission; (ii) VOC emission rates are light-dependent and subject to strong diurnal variation due to the close relationship between VOC production and photosynthesis; (iii) the VOC emission potential (emissions under standardized environmental conditions) varies with the season: increase during development with a maximum during the period of highest physiological activity in summer to a senescence-dependent decrease in autumn; and (iv) the importance of VOC emissions from sugarcane exceeds the impact of other major bioenergy and crop species on regional air chemistry and GHG production.

2. Materials and methods

2.1. Plant materials and growth conditions

Seeds of *Saccharum officinarum* L. cultivar "Q232" were purchased from a commercial institute (Australian Sugarcane Research Institute: BSES Ltd., Indooroopilly, Queensland, Australia). The cultivar Q232 is a cross between Australian indigenous *S. officinarum* × *S. spontaneum* cultivars, with resistance to typical sugarcane diseases (*e.g.,* cereal blight, red rust and root rot), acclimation to cold and poor soil nutrition, and rapid growth with a 12-months growing season.

Sugarcane seeds were planted in a greenhouse in square plastic pots (9 × 9 × 11 cm) at the end of January 2010, each containing 0.6 L of autoclaved soil substrate prepared by mixing commercial soil (Floradur A 0.8; Floragard Vertrieb GmbH, Oldenburg), sand (quartz sand, medium coarse; Glaser Trockensand GmbH, Malsch) and Perlite (Perligran 2/6, Knauf Perlite) in a ratio of 60:35:5. During the first weeks of cultivation, a hood covered with UV-transparent plastic film was placed inside the greenhouse to optimize the growth conditions of the young sugar cane seedlings. In addition, the substrate contained 1.5 *g* of

commercial NPK permanent fertilizer in each pot (Basacote Plus 6 M 16 + 8 + 12 (+2); Compo GmbH & CoKG, Münster, Germany; 2.5 *g* L^{-1} grows substrate). Seedlings at the 2nd- or 3rd-leaf stage (BBCH code: 1.2–3, (Lancashire et al., 1991) were transplanted into plastic pots on the 01st, February 2010, with 7 L of the soil substrate mixture described above and 35 *g* of the commercial NPK fertilizer Basacote Plus (5 *g* L^{-1} soil substrate). After 5 months of cultivation, all sugarcane seedlings were re-potted into plastic pots containing 14 L of soil substrate and 70 *g* of NPK fertilizer Basacote Plus (5 *g* L^{-1} soil substrate) and cords were carefully tied around the top of each plant to ensure their stability. After 8 months of cultivation, each sugarcane plant was additionally fertilized weekly with the commercial fertilizer Hakaphos blue (Bayer, Leverkusen, Germany; 3 *g* L^{-1}; 100 mL $plant^{-1}$). Throughout the entire growing season, sugarcane seedlings were watered regularly with tap water to keep the growth substrate moist without soaking to ensure adequate water supply of the plants.

To mimic the environmental conditions outside, the sunlight entering the greenhouse was supplemented by sodium vapor lamps (SON-T AGRO 400 W, Philips. Germany) to maintain the radiation intensity between 400 and 700 μmol photons m^{-2} s^{-1} photosynthetic active radiation (PAR) between 6:30 h and 18:30 h. The air temperature in the greenhouse was regulated by heating in the cooler season (October to mid-May). When the room temperature exceeded 30℃, shading and ventilation by the automatic external sun blinds and side vents were used. The ambient air temperature in the greenhouse was maintained between 15 and 38℃, within the tolerant temperature range of sugarcane (Ebrahim et al., 1998; Ebrahim et al., 1998; Du et al., 1999). The climatic conditions in the greenhouse during the experimental period are shown in Supplementary Table S1;Fig. S3a.

2.2. Measurements

2.2.1. Plant growth

Five sugarcane seedlings were randomly selected (n = 5) and the length of the main shoot and the number of leaves were measured and recorded monthly across the whole growing season. Plant height was defined as the height of the main shoot from pot soil surface to the top of the highest leaf. For determining the number of leaves, only leaves with fully-spread leaf blades were considered. In addition, only leaves, healthy and green by visual inspection, were included into the analysis.

Plant biomass accumulation was determined for three age classes of sugarcane plants, *i.e.,* 3 M: young plants (after 3 months cultivation) with fully unfolded, fast-growing and bright green colored leaves, 7 M: mature plants (after 7 months cultivation) with green colored and fully-expanded mature leaves, and 11 M: senescent plants (after 11 months cultivation) with wilted-tips, brown and yellow edge-colored leaves. For this purpose, five sugarcane plants (n = 5) with similar growth characteristics were randomly selected at each of these growth stages. After the main shoot height and the number of leaves of each plant were determined, above-ground tissues were collected, separated into shoots and leaves and weighted (fresh weight, FW). The leaf area of every shoot was determined using a scanner (CanonScan Lide 70, Canon, Amsterdam, the Netherlands) and an image analyzer software (GSA Image Analyser, GSA GmbH, Rostock, Germany).

All collected plant tissues were dried in the oven at 65℃ to weight constancy for dry weight (DW) determination. Water content (WC) was calculated as the difference between fresh weight (FW) and dry weight (DW) in relation to FW and expressed as percentage based on the following equation:

$$WC(\%) = \frac{FW - DW}{FW} \times 100\% \quad (1)$$

From these data, total plant leaf area was calculated using the general relationship between leaf area (LA) and leaf dry weight (LDW) (Robison and Massengale, 1967; Wolf et al., 1972). For the calculation of specific leaf area (SLA) of sugarcane, leaf area (m^2) was divided by dry weight of leaf (DW, kg) according to:

$$SLA = \frac{Leafarea(m^2)}{DWofleaf(kg)} \quad (2)$$

2.2.2. CO_2 and H_2O gas exchange

CO_2 and H_2O gas exchange were determined on three fully-expanded leaves of each of the five sugarcane plants (n = 5) used for biomass analysis in three age classes (see above) of sugarcane plants during the daylight hours between 10:00 h and 16:00 h with a portable gas exchange measurement system (GFS 3000, Walz, Effeltrich, Germany) as previously described (Hu et al., 2018). At each plant age-class investigated (3 M: young plant after 3 months cultivation, 7 M: mature plant after 7 months cultivation, and 11 M: senescent plant after 11 months cultivation, respectively), three leaves of each plant were used to determine the gas exchange characteristics, *i.e.,* for young (3 M) plants: young leaves with fully unfolded, fast-growing and bright green color; for mature (7 M) plants: mature leaves green colored and fully-expanded, and senescent (11 M) plants: senescent leaves with wilted-tips, brown and yellow edge-color. To allow for VOC emission analyses with the same gas exchange system, the original tubing was replaced by chemically inert perfluoralkoxy alkane (PFA) tubes (Sigma-Aldrich, Munich, Germany) (Fig. S1). For measurements, intact leaves attached to the plants were placed into an 8 cm^2 leaf cuvette and flushed with ambient air at 941 mL min^{-1}. Leaf temperature (30℃), relative humidity (60 %), CO_2 concentration (400 μmol mol^{-1}) and light intensity (1,000 μmol $m^{-2}s^{-1}$ photosynthetic active radiation (PAR)) were kept constant during the measurements. Following the 20 min adaptation period, the net rate of photosynthesis (P_n), stomatal conductance (G_s) and transpiration rate (T_r) were determined. Intrinsic water-use efficiency (iWUE) was calculated as the ratio between P_n and G_s.

In general, the diurnal fluctuations of air temperature in the greenhouse were greater during the measurement of young and mature plants (*i.e.,* from mid of May to mid of September 2010) than during the measurements of senescent plants (Table S1). During the whole cultivation period, diurnal fluctuations of relative humidity in the greenhouse were in the range of 30.6 % to 97.3 %. Daily average humidity varied from 51 % to 66 %, with higher humidity and greater humidity fluctuations in summer (Table S1).

2.2.3. VOC analysis

VOC emissions were determined with two techniques (Fig. S1): "offline" analysis was ensured by accumulation of leaf emitted VOCs on adsorber tubes followed by GC–MS analysis. This technique allows for determination of a wide range of emitted volatiles but at a low temporal resolution (here: 60 min). In contrast, the complementary "online" analysis with a high-sensitive proton-transfer-reaction mass spectrometer (PTR-MS) instrument provided close to real-time data (temporal resolution of seconds) but only masses of volatiles are monitored, which makes compound identification more difficult. For example, emission of mass 69 was detected which equals to the protonated mass of isoprene. However, as GC–MS analysis clearly indicated that isoprene was not emitted, mass 69 must result from another, yet not identified gas. We therefore indicate this gas in results/discussion as "VOC69" and not as isoprene. VOC sampling with both approaches took place during the day, with a break at noon, between 10:00 h and 16:00 h (exceptions: daily courses). Before each measurement, leaves were placed into the 8-cm^2 leaf cuvette of the gas exchange measurement system, and after an adaptation period of 20 min, sampling started. The experimental information of both GC–MS and PTR-MS methods related to VOC measurements were given in Table S2.

For the GC–MS approach, an adsorption tube together with an air sampling pump (pocket pump, Siko, Buchenbach, Germany) was attached to the exit of the leaf cuvette (see scheme in Supplemental material). At a flow rate of 100 mL min^{-1} (11.44 % of the total gas flow

through the measuring cuvette), air exiting the leaf cuvette was channeled over this adsorber tube for 60 min, resulting in a total volume of 6 L cuvette air which was analyzed for VOCs. The VOC adsorbing tubes (Twister desorption liner, Gerstel GmbH & Co.KG, Mülheim, Germany) were packed with 30 mg Tenax TA (60/80 mesh) and 40 mg Carbotrap (20/40 mesh) (Supelco, Bellafonte, PA, USA) separated by silanized glass wool. After the experiment, they were stored at 4 °C until analysis which usually occurred within the same week.

VOCs accumulated on adsorber tubes 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) as previously described (Hu et al., 2018). For thermodesorption of volatiles, the adsorber tubes were heated to 240℃ and the released VOCs were cryofocused at −100℃ in the CIS. After heating the CIS to 240℃, the desorbed VOCs were channeled onto the separation column (DB-624, length 60 m, id. 0.25 mm, 1.4 μm film thickness, Agilent Technologies, Böblingen, Germany). The GC oven temperature program started at 40℃, increased at a rate of 6℃ min^{-1} until 100℃ and subsequently at 16℃ min^{-1} until 230℃. The MSD was run at standard settings provided earlier (Kreuzwieser et al., 2021). Peak identification, peak alignment and manual re-integration of badly integrated peaks was done with the MassHunter software (Agilent). For peak identification, the observed spectra were compared with the NIST database and some external standards (mainly for terpenes and isoprene) (Hu et al., 2018; Welle et al., 2021; Winters et al., 2009) which were analyzed under the same conditions than the samples. Due to a lack of most authentic standards for the compounds identified, relative emission rates were calculated (*i.e.,* signal abundances were used without calculation of the amounts of compounds). For this purpose, we subtracted the peak areas of the compounds found in the empty leaf cuvette from the leaf containing cuvette peak areas. Furthermore, we accounted for the flow rates through the cuvette and onto the adsorber tube, and the leaf area (8 cm^2) in the cuvette.

To investigate diurnal patterns of VOC emission by real time analyses, part of the air leaving the leaf cuvette (100 mL min^{-1}) was channeled into a proton transfer reaction mass spectrometer (PTR-MS; Ionicon Analytic, Innsbruck, Austria). As for GC–MS analysis of VOCs, the portable gas exchange measurement system (GFS 3000, Walz, Effeltrich, Germany) was operated as described above. However, to minimize background signals, we channeled synthetic air (synthetic air 5.0, Air Liquid, Düsseldorf, Germany) into the system. Each measurement started at 04:00 h under dark conditions and was continued until noon next day. The light was switched on at 06:00 h. At daytime, the radiation intensity was set to 1,000 μmol $m^{-2}s^{-1}$ PAR. Thus, datasets from 04:00 h to 06:00 h and from 10:00 h to 12:00 h were used for calculation of mean night and daytime VOC emissions of sugarcane leaves, respectively. The PTR-MS operating parameters were E/N = 110 Td (where E is the electric field; N the buffer gas number density), p-drift = 1.73 mbar, T = 43℃, V = 400, O_2^+ and NO^+ < 2 % of H_3O^+. The low E/N ratio was maintained in order to minimize fragmentation of monoterpenes as described by (Ghirardo et al., 2010). Conditions in the ion source were further adjusted that the ratio of oxygen ions to primary ions was below 2. The resulting primary ion signal was at least $5*10^6$ cps. Under the given conditions, the H_3O + ions form water clusters at masses M37 + and M55 + are considered (and calculated) as part of the primary ion signal as modified from (Tani et al., 2004). The raw data (counts per second, cps) of a given VOC were normalized to standard conditions of 10^6 primary ions and a pressure of 2.03 mbar in the reaction tube (ncps, normalized counts per second):

$$VOC[ncps] = \frac{VOC[cps]*10^6}{(M21[cps] + M37[cps] + M55[cps]} * \frac{2.03[mbar]}{p - drift[mbar]} \quad (3)$$

We furthermore ran calibration curves with authentic standards (isoprene, acetaldehyde, α-pinene, methanol) (1 ppm of each gas in N_2, Apel-Riemer Environmental Inc., Colorado, USA). Because our calibration gas mixture did not contain ethanol, we used the methanol calibration factor for calculation of ethanol concentrations. Acetaldehyde, isoprene, monoterpene and oxygenated OVOCs, *i.e.,* methanol, ethanol and LOX products, were selected as targeted VOCs since they are known to play an important role in other grass and crop species (Fukui and Doskey, 2000; König et al., 1995; Kirstine et al., 1998). As mentioned above, GC–MS analysis did not reveal emission of isoprene from leaves as seen in other grasses (Fall et al., 2001; Wiß et al., 2017). We therefore decided to name the compound detected at mass 69 (protonated mass 68) not isoprene but "VOC69".

2.3. Statistical analysis

For statistical difference determination of plant biomass, water content, CO_2 and H_2O gas exchange, and VOC emission across diurnal courses (*i.e.,* day and night) and/or plant developmental stages (*i.e.,* young, mature and senescent stages), data were first tested by either Kolmogorov-Smirnov or Shapiro-Wilk tests for normal distribution. Where necessary, data were transformed using either log- or square-root transformation to satisfy the assumptions of normality and variance. Significant differences between day and night were assessed by using the paired Student's *t*-test. Significant differences between young, mature and senescent stages of sugarcane plants were assessed by using one-way analyses of variance (one-way ANOVA) followed by Tukey *post hoc* tests. Differences were considered statistically significant at $p < 0.050$. All statistical analyses were performed using Sigmaplot 14.0 (Systat Software GmbH, Erkrath, Germany).

2.4. Modelling and further analyses

To investigate the influences of PAR and temperature on CO_2 and H_2O gas exchange as well as VOC emissions, either PAR intensity or temperature inside the leaf cuvette were modified, while all other parameters were maintained at standard conditions (see above). We tested a range of temperatures between 20 and 45℃ in steps of one degree, and radiation between 0 and 1945 μmol m^{-2} s^{-1} in variable intervals increasing from 10 to 100, according to previously reported tolerance ranges (Ebrahim et al., 1998; Ebrahim et al., 1998; Clements, 1980).

Net photosynthesis (P_n) dependence on PAR (μmol (photons) m^{-2} s^{-1}) was described with a modified Michaelis-Menten equation, first proposed by Baly (Baly, 1935):

$$P_n = \frac{\Phi PARA_{max}}{\Phi PAR + A_{max}} - R_D \quad (4)$$

With Φ being the quantum yield in the dark (μmol (CO_2) μmol (photons) $^{-1}$), A_{max} is maximum gross photosynthesis, and R_D is dark respiration (both in μmol (CO_2) m^{-2} s^{-1}). For other exponential relationships (*e.g.,* transpiration, stomatal conductance, and water use efficiency), a simple relationship of the form X = Pm PAR / (km + PAR) has been fitted to data. With Pm being the maximum value and km representing the PAR value where Pm/2 is reached.

VOC emissions (E) are represented as principally dependent on light as well as temperature:

$$E = E_s f_L CL + E_s(1 - f_L)CTM \quad (5)$$

With *CL* being the light- and *CTM* being the temperature dependence algorithms, f_L being the light dependent fraction, and E_s are standard emission rates − which are defined to be the emission rate at 1000 μmol $m^{-2}s^{-1}$ PAR and 30℃. For the description of VOC emissions in dependence on temperature (CTM term in Eq. (5), an equation proposed in Guenther (Guenther et al., 1993) was applied. Since this algorithm assumes that compound release depends on tissue conductance only, emission can be described as:

$$CTM = exp[\beta(T - T_S)]$$

using a standard temperature of 303.15 K (30℃) as well as the coefficient (β), which is derived specifically for each compound. In case light dependency could be detected, emission (C_L) is described additional by the response of enzymatic activity to light as proposed in Guenther (Guenther et al., 1993):

$$CL = \frac{\alpha c_{L1} PAR}{\sqrt{1 + \alpha^2 PAR^2}} \quad (7)$$

With α = 0.0027, and c_{L1} = 1.066. In case light as well as temperature dependent emission occur, f_L is larger than 0. The determination of the light dependent fraction has been done by regression analysis between the observed emission rates and the function *CL*.

For estimating the atmospheric reactivity of the VOCs emitted, velocity constants for the reaction of the different VOCs with atmospheric OH radicals (k(OH + VOC; 25℃)) were adapted to calculate the specific OH reactivity of the VOCs emitted as described in (Hu et al., 2018). These values were used to calculate the approximate atmospheric lifetime of individual VOCs. For this purpose, a constant atmospheric OH radical concentration of 1.5 × 10^6 $OH^{\cdot}$ cm^{-3} was assumed for 12 h per day (Lawrence et al., 2001; Seinfeld and Pandis, 2016). The calculations were carried out with the AopWin™ module of the EPI Suite™ software package (https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface, EPA, USA).

3. Results

3.1. Growth and development of sugarcane plants

During the four-month intervals between the developmental stages analyzed, above-ground biomass (shoots and leaves), leaf number and height of sugarcane plants increased significantly (Table 1, Fig. S2). The water content of sugarcane leaves decreased during the growing season and was almost 20 % lower in senescent compared to young plants. On the other hand, the water content of the shoots increased by about 10 % from young to mature plants and afterwards remained constant (Table 1).

3.2. CO_2 and H_2O gas exchange at different plant developmental stages

Across the plant developmental stages studied, the highest foliar net rates of photosynthesis (P_n), transpiration rate (T_r) and stomatal conductance (G_s) were observed in young and mature plants after 3- and 7-months growth. In plants after 11-months growth with leaves showing wilted-tips, brown and yellow edge-color (hereafter described as senescent plants), foliar P_n, T_r and G_s significantly declined (Fig. 1a-c). The decline in G_s resulted in an increased water vapor pressure deficit between the intercellular spaces of the senescent leaves and the surrounding air (Fig. 1d). However, the intrinsic water-use efficiency (iWUE) was similar across plant developmental stages (4.9 ± 0.4, 5.1 ± 0.4 and 5.2 ± 0.4 μmol CO_2 (mmol H_2O)$^{-1}$, in young, mature and senescent plants, respectively).

Table 1
Above-ground biomass accumulation at different developmental stages of sugarcane plants.

	Harvest 1	Harvest 2	Harvest 3
Plant age [months]	**Young (3 M)**	**Mature (7 M)**	Senescent (11 M)
Shoot height [cm]	95.0 ± 10.2a	200.8 ± 34.6b	284.8 ± 19.3c
FW plant^{-1} [g]	150.1 ± 18.8a	400.6 ± 37.6b	743.2 ± 97.9c
DW plant^{-1} [g]	59.4 ± 5.8a	126.7 ± 12.7b	224.3 ± 34.7c
Water contents [%]	60.2 ± 4.6a	68.3 ± 3.2b	69.9 ± 1.4b
Number of leaves [Plant^{-1}]	8.4 ± 0.5a	13.8 ± 0.8b	21.4 ± 1.8c
FW leaf^{-1} [g]	35.7 ± 2.7a	88.3 ± 10.4b	121.2 ± 14.2c
DW leaf^{-1} [g]	4.9 ± 0.4a	17.4 ± 3.2b	34.0 ± 2.8c
Water content of leaf [%]	86.3 ± 1.0a	80.3 ± 3.3b	71.8 ± 3.1c
Leaf area [dm^2/plant]	6.4 ± 0.5a	22.8 ± 4.2b	44.5 ± 3.6c

For plant biometric results: Shoot height, number of leaves, as well as fresh (FW) and dry weight (DW) of these tissues were determined in young, mature and senescent plants after 3, 7, and 11 months of cultivation, respectively. The leaf DW was used to calculate total leaf area per plant. Data shown are means ± SD (n = 5). Significant differences between developmental stages are indicated by different small letters ($p < 0.05$).

3.3. VOC emission at different plant developmental stages

Our GC–MS and PTR-MS analyses indicated that a total of 40 different VOCs of seven chemical classes (*i.e.,* alkanes, alkenes, aromatics, aldehydes, alcohols, ketones and terpenoids) were emitted from sugarcane leaves across the plant developmental stages. They were separated into four groups, *i.e.,* non-terpenoid aliphatic compounds, aromatic compounds, terpenoids, and oxygenated VOCs (OVOCs) including lipid oxidation (LOX) products (Fig. 2a). Among the VOCs identified, alkanes and alkenes were significantly represented in the emission profiles and were combined in the group of non-terpenoid aliphatic compounds (Table S3). The emitted sulfur (S)-containing compound 3-methylthiophene has aromatic characteristics and was combined with six aromatic benzenoids (Fig. 2a; Table S3). The monoterpenes bornylene, p-cymene and δ-3-carene and the monoterpenoid β-ionone were combined in the group of terpenoids. Three typical LOX products were identified, *i.e.,* the aldehyde n-hexanal and the alcohols (Z)-3-hexen-1-ol and 1-hexanol. A total of four aldehydes, three alcohols and two ketones were emitted and combined in the group of OVOCs. Isoprene emission was not detected at all the developmental stages studied (Fig. 2a; Table S3). Across plant development stages (*i.e.,* from 3 M to 7 M and to 11 M), the numbers of quantified VOCs decreased from 34 (young plant) to 21 (mature plant), and to 3 (senescent plant), respectively (Fig. 2a). The emission groups with the strongest reduction were non-terpenoid aliphatic and aromatic compounds. Independent of age, most emitted VOC compounds belong to the groups of OVOCs and non-terpenoid aliphatic compounds (Fig. 2a).

The amounts of VOCs emitted were estimated from the peak areas of the total ion chromatograms (TIC). Based on this estimation, the highest emission of OVOCs occurred in mature and senescent plants (Fig. 2b; Table S3). Despite the significantly reduced number of VOCs emitted compared to young plants (reduction by 40 %), the total amount of VOCs emitted by mature plants was estimated to be ca. 4-fold higher compared to young plants ($p < 0.001$), indicating opposite patterns of emission composition diversity and quantity between young and mature plants (Fig. 2a-b, Table S3). The increase in total VOC emission during plant development was mostly due to OVOCs (ca. 4-fold) and non-terpenoid aliphatics (ca. 3.5-fold). In senescent plants, a significant reduction in total VOC emissions compared to young ($p < 0.001$) and mature plants ($p = 0.02$) was caused by all identified VOC groups (Fig. 2a-b; Table S3).

3.4. Diurnal variation of CO_2 and H_2O gas exchange and VOC emission

Due to the missing light energy, CO_2 and H_2O gas exchange of mature leaves on mature sugarcane plants showed hardly any P_n, T_r and G_s during night. Slightly negative values of P_n were attributed to dark respiration (Table 2). Upon transition from night to daytime, P_n, T_r and G_s immediately increased and daytime levels were reached after ca. 2 h (Fig. S6).

To obtain detailed information on diurnal changes of VOC emissions, real time analyses were performed by continuous PTR-MS measurements. With this approach, significant emissions of six VOCs were recorded at night (Fig. 2c). Overall, VOC emissions were dominated by methanol and acetaldehyde. In addition, methanol emissions indicated of ca. 4-fold (day) and 5-fold (night) higher than acetaldehyde emissions, respectively (Fig. 2c). The emission rates of the other four VOCs (*i.e.,* LOX, monoterpene, ethanol and VOC69) were one order of magnitude

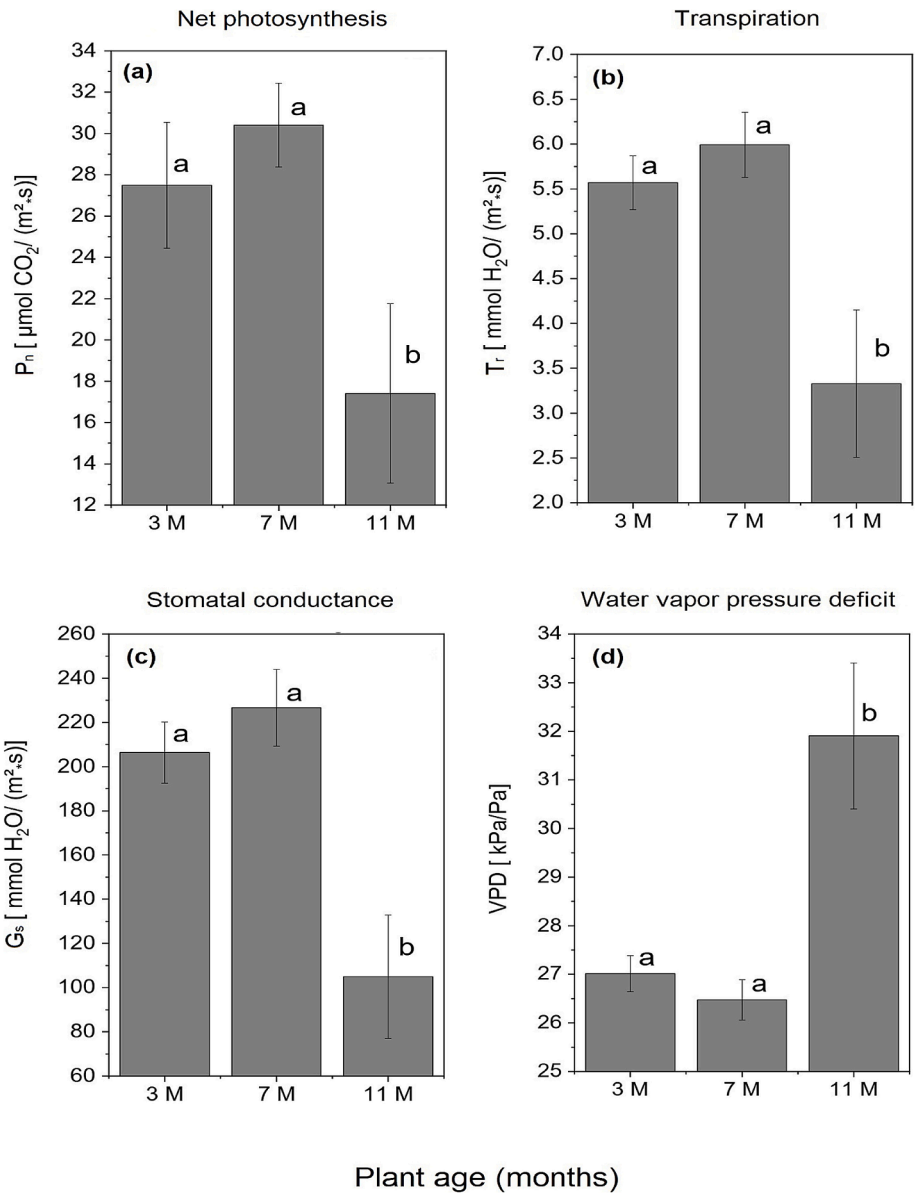

Fig. 1. CO_2 and H_2O gas exchange of sugarcane at different plant developmental stages during the growing season. Data shown are means ± SD (n = 5). Significant differences of each gas exchange parameter between developmental stages are indicated by different small letters ($p < 0.05$). Measurements were performed at the daylight hours between 10:00 h and 16:00 h.

lower compared to methanol and acetaldehyde and did not differ statistically between each other ($p > 0.05$; Fig. 2c).

Transition from night to daytime greatly increased VOC emissions except for methanol and reached a constant level of ethanol, acetaldehyde and monoterpene emission within one hour. This increase amounted to 42.3 ± 5.3 %, 71.5 ± 7.1 % and 84.4 ± 5.2 % for ethanol, acetaldehyde and monoterpenes, respectively (Fig. 2). In contrast, average emission rates of methanol were significantly lower during daytime compared to the night, despite an initial increase upon night to day transition (Fig. 2c, 3). Emissions rates of LOX and VOC69 were highest at daytime in the morning after night to day transition, with an increase by ca. + 70 % compared to average emissions during the night. However, emission rates of both VOCs subsequently decreased during daytime to the rates observed during night (Fig. 3).

3.5. CO_2 and H_2O gas exchange dependence on PAR and temperature

The relation between PAR and gas exchange parameters could be well represented with Michaelis-Menten algorithms. The relation between measurements and estimates was highly significant ($p < 0.001$) ($R^2(P_n) = 0.970$, $R^2(T_r) = 0.976$). The relationship between P_n and PAR indicates that saturation had not yet fully been reached at the highest PAR intensity applied. According to the regression model used, saturation was reached at 1950 µmol $m^{-2}s^{-1}$ PAR. At light saturation, an average rate of 34.1 ± 4.6 µmol CO_2 $m^{-2}s^{-1}$ was calculated for P_n and the light compensation point was reached at 12.2 ± 4.2 µmol $m^{-2}s^{-1}$ PAR (Fig. 4a). For more details see supporting text and Fig. S4 in the Supplementary file.

Photosynthesis showed an optimum relation to temperature with a relatively broad maximum between 27 and 42 °C and a relatively steep decline afterwards. In contrast, conductivity displayed a minimum in approximately the same temperature range (26 to 39 °C). Transpiration showed an exponential development with increasing temperature which is likely related to the similarly increasing vapor pressure deficit (Fig. 5).

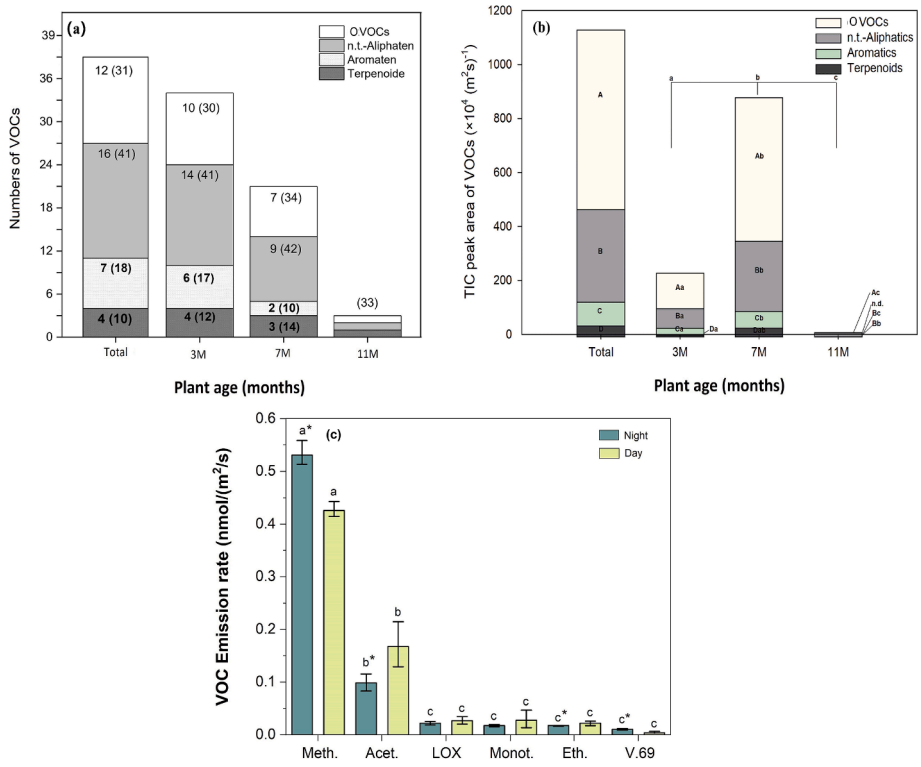

Fig. 2. Diversity and composition of VOCs (a), total ion chromatogram (TIC) peak areas (b) of VOCs emissions from sugarcane at different plant developmental stages during the growing season, and average emission rates of VOCs from mature leaves of mature sugarcane plants (7-months-old) during night (04:00 h to 06:00 h) and day (10:00 h to 12:00 h) (c). (a): The VOCs emitted from leaves of young (3 M), mature (7 M) and senescent (11 M) sugarcane plants were divided into groups based on their chemical properties and biological significance. The numbers of VOCs emitted of each group at different developmental stages are indicated in the bars. The values in the parentheses represent the percentages of each VOC group on the total number of VOCs emitted at each developmental stage. n.t. −Aliphatics: non-terpenoid aliphatics; OVOCs, oxidized VOCs, (b): The peak areas of each group of VOCs were summarized up. Statistically significant differences between the determined peak areas of each VOC group and summary of four groups among different leaf age classes are indicated by different small letters ($p < 0.05$). Statistically significant differences among the VOC groups are indicated by the different capital letters ($p < 0.05$). n.d.: not detected, (c): The data shown are means ± SD (n = 5). Significant differences of emission rates for each VOC compound between day and night are indicated by * for $p < 0.05$. Different capital or small letters indicate significant differences between the emission rates of different VOCs during day or night ($p < 0.05$). Acet.: acetaldehyde, Eth.: ethanol, LOX: fatty acid derivatives, Meth.: methanol, Monot.: monoterpene, V.69: VOC69. Note. Data for panels a-b were derived from GC–MS analysis after accumulation of VOCs on adsorber tubes; data from panel c were derived from online PTR-MS detection for diurnal variations of VOC emission of 7-month-old sugarcane plants.

Table 2
Day and night CO_2 and H_2O gas exchange of mature sugarcane plants (7-months-old).

Parameter		Unit	Night		Day
P_n	net photosynthesis	[μmol CO_2/(m^2*s)]	−0.63 ± 0.34	***	30.01 ± 3.36
T_r	transpiration	[mmol H_2O/(m^2*s)]	0.08 ± 0.03	***	5.88 ± 0.72
G_s	stomatal conductance	[mmol H_2O/(m^2*s)]	2.39 ± 0.76	***	218.2 ± 39.3
VPD	water vapour pressure deficit	[Pa/kPa]	34.15 ± 0.94	***	27.16 ± 1.75
C_i	intercellular CO_2 concentration	[ppm]	848.9 ± 351.0	***	133.9 ± 10.4
iWUE	water use efficiency	[μmol CO_2/mmol H_2O]	−9.12 ± 6.85	***	5.11 ± 0.17

For gas exchange: The mean values were calculated from the parameter values measured between 04:00 h and 06:00 h (night) and between 10:00 h and 12:00 h (day). Data shown are means ± SD (n = 5). Statistically significant differences of each parameter between day and night are indicated by * for $p < 0.05$, by ** for $p < 0.01$ and by *** for $p < 0.001$.

3.6. VOC emission dependence on PAR and temperature

Temperature and light are commonly viewed as key environmental factors controlling BVOC emissions, as previously reported for other species, *e.g.,* Norway Spruce (Huang et al., 2018). Therefore, we tested the dependency of the major emission types of sugarcane for such dependencies. Already the results of diurnal measurements suggested a certain positive correlation between PAR and ethanol emission (R^2(Ethanol) = 0.380; Fig. S4e), whereas other VOC emissions, *e.g.,* LOX, monoterpenes, VOC69 and methanol seemed to be independent of PAR intensity (Fig. 3, S3). Correlation analysis confirmed the independency of the emissions of methanol, LOX, monoterpenes and VOC69 from PAR (R^2(Meth) = 0.016; R^2(LOX) = 0.051; R^2(Mono) = 0.036; R^2(VOC69) = 0.040, respectively). For more details see Fig. S4a-d in the Supplementary file.

For ethanol, a standard emission rate of 0.0192 nmol $m^{-2}s^{-1}$ (25.86 ± 0.7 ng g^{-1} DW h^{-1}) has been derived from the light curve measurements. The fraction that is temperature dependent (emission rate in the dark at 30℃) is 0.0117 nmol $m^{-2}s^{-1}$ which is 61 % of the standard emission (dashed line in Fig. 6). The additional light response could be described with the algorithm for enzyme kinetics with high accuracy (R^2 = 0.963) considering only 39 % of the standard rate (0.0075 ± 0.0005 nmol $m^{-2}s^{-1}$) as light dependent (pointed line in Fig. 6). It should be noted that the light-curve experiments differed somewhat from the

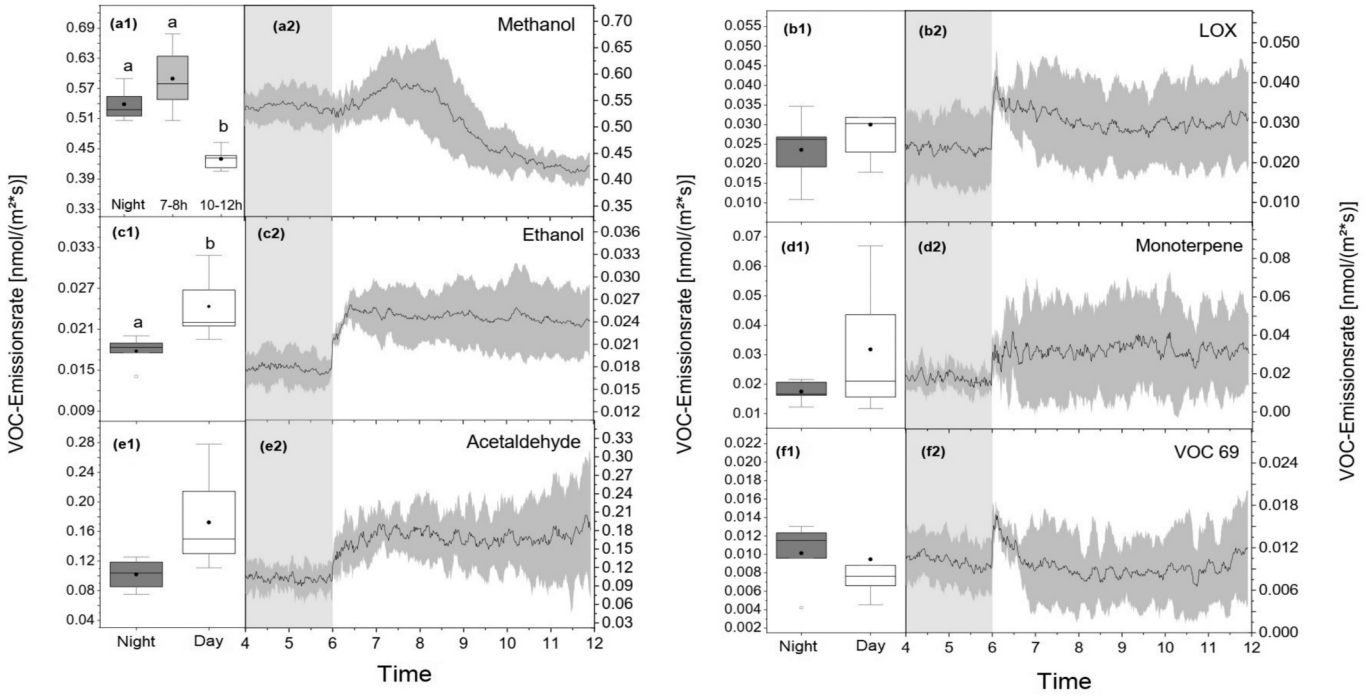

Fig. 3. Diurnal changes in standard VOC emission factor from leaves of mature sugarcane plants (7-months-old) as derived from PTR-MS analysis. a1-f1: Averaged data for the night recorded between 04:00 h to 06:00 h (T = 30℃, PAR = 0 µmol m^{-2} s^{-1}) and for the day between 10:00 h to 12:00 h (T = 30℃, PAR = 1000 µ m^{-2} s^{-1}); (n = 5) with 25/ 75th percentile ± 1.5x interquartile distance (whisker); points indicate the mean, bars the median, and open squares measured values that deviate from the mean (outliers). For methanol, an additional emission average was calculated for the time between 07:00 h and 08:00 h. Statistically significant differences between night and day are indicated by different small letters ($p < 0.05$). a2-f2: Fluctuation of VOC EF (means ± SD, n = 5) during the whole investigation period.

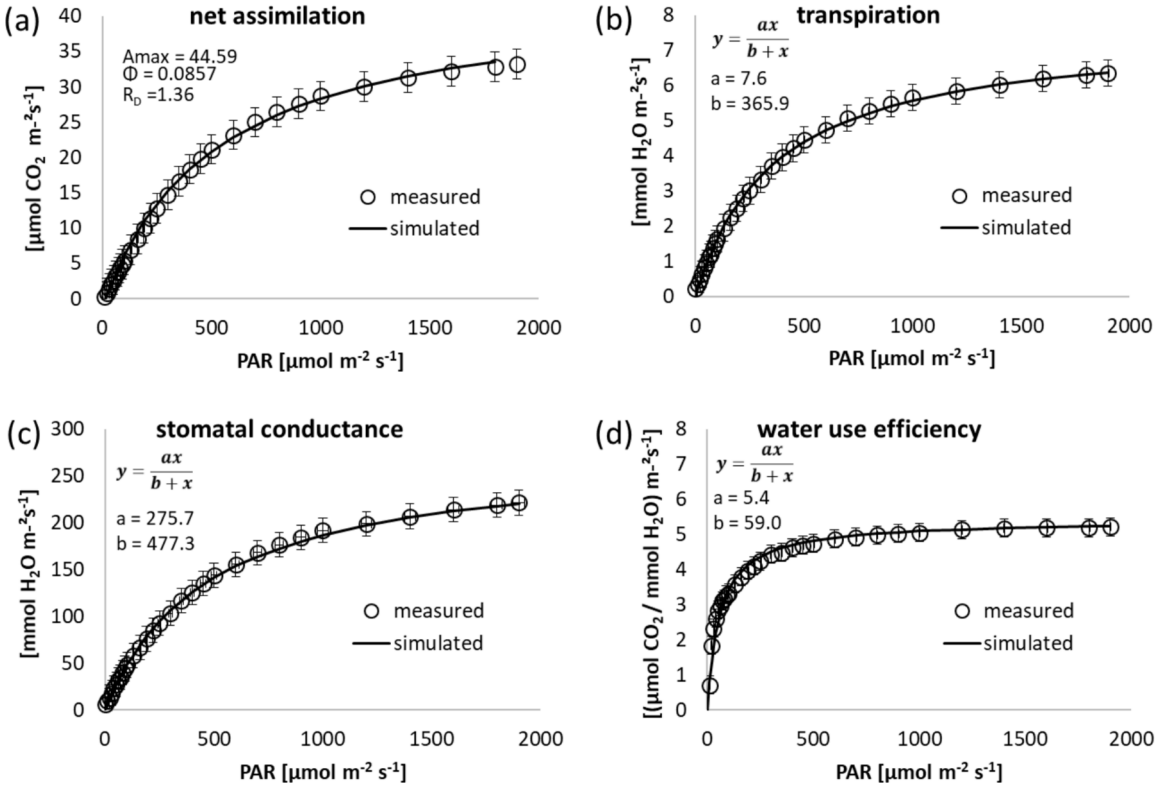

Fig. 4. CO_2 and H_2O gas exchange as well as related variables in dependence on PAR from leaves of mature sugarcane plants (8-months-old). In panel (a) simulated net photosynthesis as calculated according to Eq. (4) is presented. In panels (b-d) regression functions and fitted parameters are placed inside the panels. The data shown are means ± SD (n = 5).

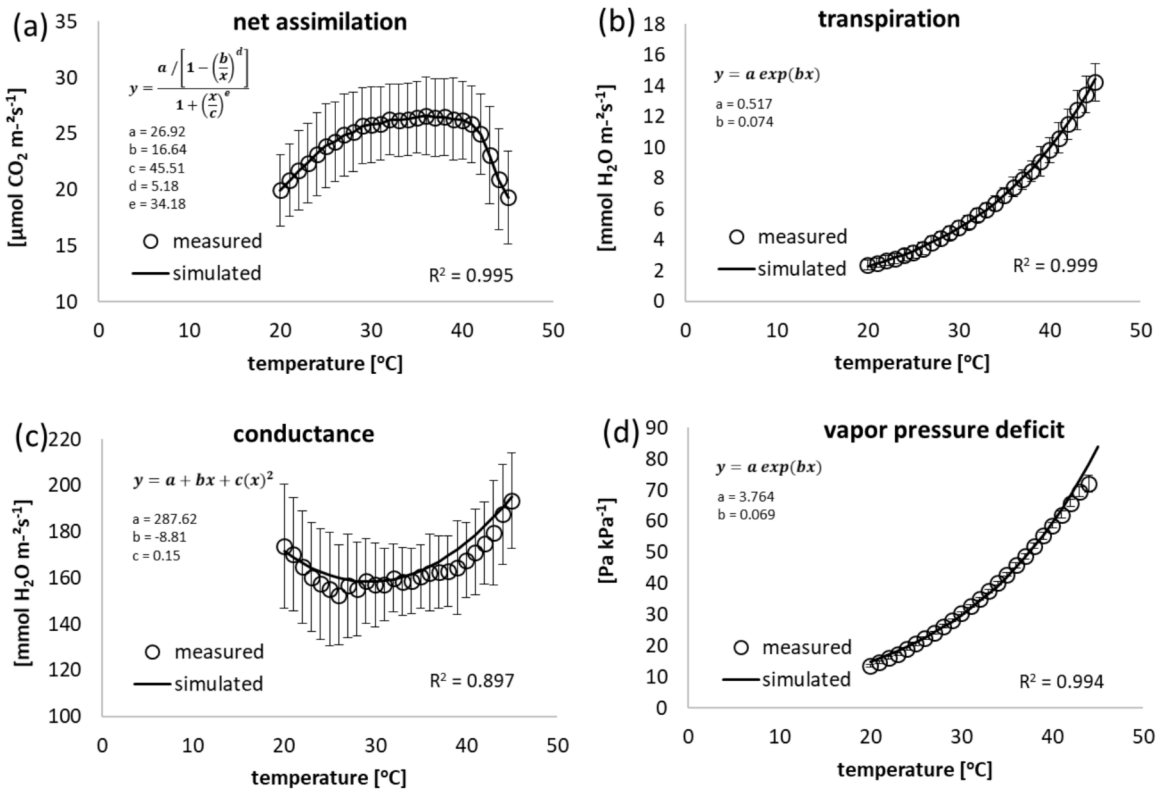

Fig. 5. CO_2 and H_2O gas exchange as well as related variables in dependence on temperature from leaves of mature sugarcane plants (8-months-old). Regression functions and fitted parameters are placed inside the panels. The data shown are means ± SD (n = 5).

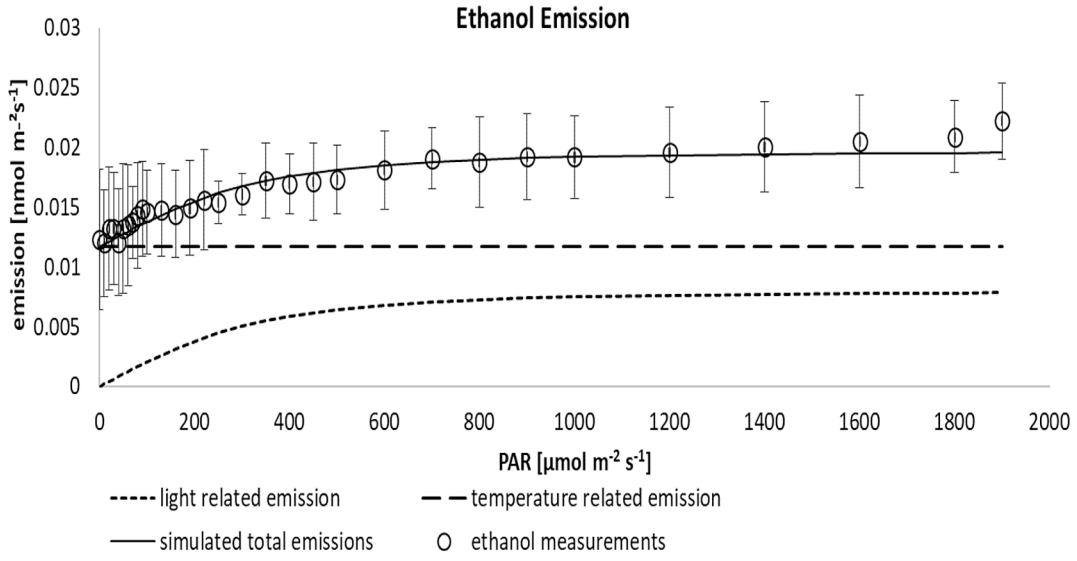

Fig. 6. Parameterized functional model between PAR and ethanol emissions from leaves of mature sugarcane plants (8-month-old). Ethanol emission was parameterized using the light dependent enzyme kinetics in conjunction with a temperature dependent storage term (according to Eq. 5–7). For emission rates (analysis via PTR-MS) and parameters see text. The results of emission measurement (E_1) are presented as points (means, n = 6) with SD.

continuous diurnal measurements, where the emissions in the night were 28 % and in the light about 8 % higher than observed under standard conditions (Fig. 3 and S6).

For all other VOCs, strong temperature dependencies could be shown, as already indicated by diurnal variations. Simulated emission response to temperature according to the temperature dependency on pool emissions (see Equation 6) strongly correlates with observed VOC emission rates (E) for all VOCs (Fig. 7). The standard emission rates (E_S) used for the regression lines and the temperature coefficients of the VOC emitted are listed in Table 3 (for derivation see Fig. S5). For all VOCs, except ethanol, there were no significant differences between E_S and the measured daily VOC emission rates during the whole growth period ($p = 0.26$; Fig. 3; Tables S3-S4). The specific temperature coefficients range from 0.030 ± 0.005 (methanol) to 0.102 ± 0.025 (LOX) and are thus somewhat different from the one suggested for general use ($\beta = 0.09$). Nevertheless, the Guenther approach for deriving emissions from

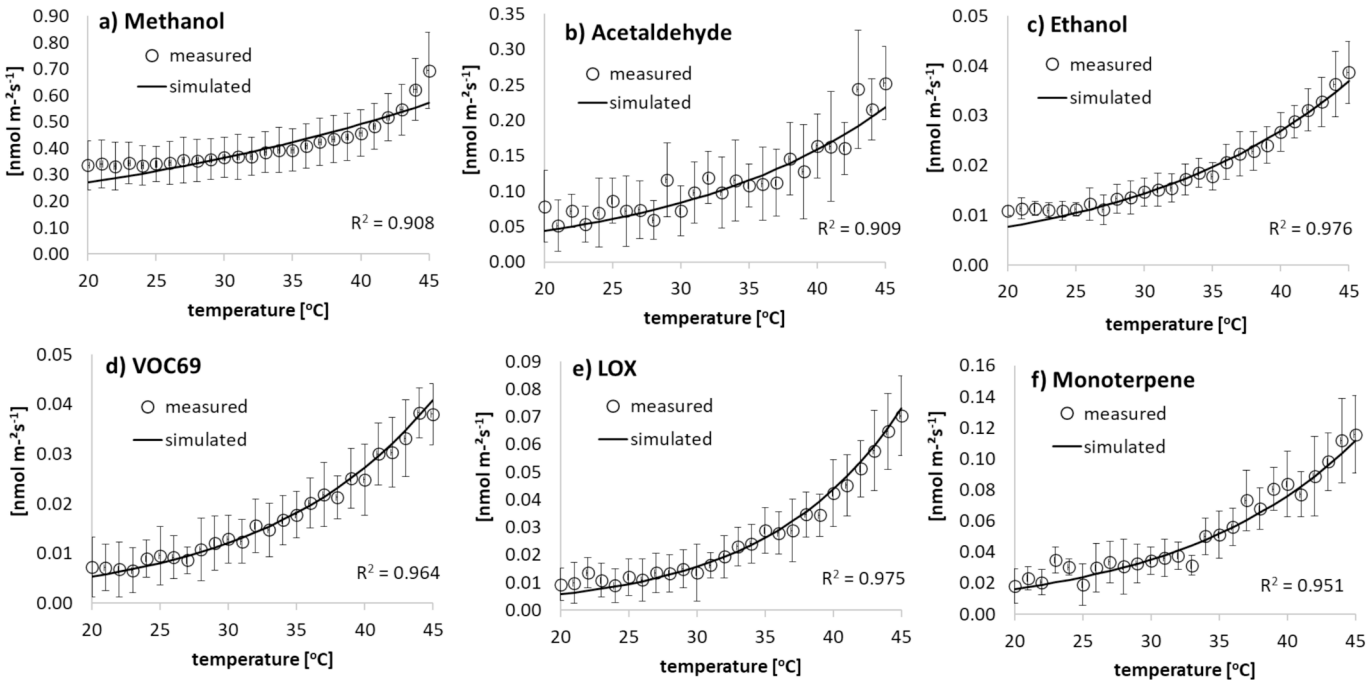

Fig. 7. Parameterized functional models between temperature and VOC emissions from sugarcane leaves. Comparison between measurements and modeled emissions ($E_G = E_S \exp(\beta (T - Ts))$, representing various emission compounds that are supposed to be temperature driven only (a-f). The results of measured emission (E) are represented as circles (means, n = 6) with SD as vertical lines. The squared coefficients (R^2) of the correlation for the modelling approach are given in the diagrams. Data shown are means ± SD (n = 5).

Table 3
Daily VOC emissions (analysis by PTR-MS), mean OH reactivity, basal emission rates and temperature coefficients of VOCs emitted from mature sugarcane plants (7-months-old).

VOC	Daily emission rates [nmol $m^{-2}s^{-1}$]	Daily emissions percentage	Atmospheric lifetime[#]	k(OH + VOC); 25C [cm^3 (Molecule × s)$^{-1}$]	Specific OH· reactivity	E_S [nmol $m^{-2}s^{-1}$]	E_S [µg g DW$^{-1}h^{-1}$]	Temperature coefficient β
Methanol	0.430 ± 0.023	62.5	25.1 days	6.16E-13	3.85E-13	0.365 ± 0.079	0.342 ± 0.073	0.030 ± 0.005
Acetaldehyde	0.172 ± 0.073	25.0	91.3 days	1.69E-13	4.23E-14	0.083 ± 0.028	0.108 ± 0.036	0.064 ± 0.017
Monoterpene	0.032 ± 0.023	4.6	2.2 hours[a]	8.36E-11[a]	3.86E-12	0.035 ± 0.006	0.140 ± 0.023	0.077 ± 0.011
LOX	0.030 ± 0.011	4.3	3.4 hours[b]	5.31E-11[b]	2.31E-12	0.016 ± 0.007	0.047 ± 0.020	0.102 ± 0.025
Ethanol	0.024 ± 0.005	3.5	4.3 days	3.58E-12	1.26E-13	0.014 ± 0.003	0.019 ± 0.004	0.063 ± 0.011
VOC69	0.009 ± 0.006	–	–	–	–	0.012 ± 0.005	0.024 ± 0.010	0.081 ± 0.025
Total (without VOC69)	0.688	100	–-	–-	6.72E-12			
Isoprene	–	–	1.8 h	1.05E-10	1.05E-10			

Daily emission rates are represented as means ± SD (n = 5). Mean daily emission rates were added up (without VOC69) and the atmospheric lifetime and specific OH· reactivity of individual VOCs was calculated. The specific OH· reactivity of VOCs was estimated by proportionally calculating the respective constant for the reaction with OH radicals (k(OH + VOC; 25C)). For comparison, the respective values for isoprene are included. #: Assuming a constant atmospheric OH· concentration of 1.5E6 molecules cm^{-3} for 12 h day^{-1}; a: from k (Bornylene x0.26, δ-3-Carene x0.73; β-Ionone x0.01), also used to calculate atmospheric lifetime; b: from k (1-hexanol x0.18, Z-3-Hexen-1-ol x0.82)), was also used to calculate atmospheric lifetime. DW: dry weight of leaves.

temperature only (EP_G) led in most cases to differences between simulations and measurements in the low temperature range (20–25 ℃).

3.7. Relation between CO_2 and H_2O gas exchange and VOC emission

For the investigation of relationships between CO_2 and H_2O gas exchange and VOC emissions, the data from three developmental stages of sugarcane plants were combined and subjected to correlation analyses (Fig. S7, Table S5). Emission rates of VOCs strongly correlated with T_r and VPD. Ethanol emissions showed the strongest correlations with these parameters (Fig. S7). Also, weak correlations between P_n/G_s and VOCs emissions were found (Fig. S7). Between the emissions of VOCs, the strongest correlations were recorded between LOX and VOC69 (r^2 = 0.618) and ethanol (r^2 = 0.607). Moderate correlations were also found between other VOC emitted, except for methanol (Table S5).

After application of elevated temperature and reestablishment of standard conditions in the leaf cuvette, P_n was significantly smaller than at the beginning of the experiment (ca. −20 %) while emission rates of LOX and VOC69 were significantly increased (+55 % and + 71 %, respectively) (Fig. S3). These results indicated damages of foliar

metabolic processes due to the elevated temperature.

3.8. OH reactivity of emitted VOCs

Daily VOC emissions from leaves of mature sugarcane plants are dominated by methanol and acetaldehyde together amounting to 87.5 % of total VOC emissions (Table 3), which possess the longest estimated atmospheric lifetime and the lowest estimated specific OH reactivity (Table 3). In addition, methanol and acetaldehyde also dominated the overall specific OH reactivity in the amounts of total daily VOC emissions (Table 3).

The different VOCs emitted from sugarcane leaves possess different velocity constants for the reaction with OH radicals (k(OH + VOC; 25C)). The most reactive VOCs were the five alkenes and three of the terpenoids emitted, with average atmospheric lifetimes ranging from 0.8 h (*β*-ionone) to 3.5 h (2,4.4 trimethyl-1-pentene) (Table S4). The emission of these reactive VOCs was generally low to moderate with larger emission rates found in mature and senescent in relation to young plants (Fig. 2b; Tables S3, S4). The other 31 identified VOCs have considerably lower velocity constants for the reaction with OH radicals. Particularly several alkanes and aromatics emitted are characterized by a relatively high atmospheric lifetime of 1 to 4 (benzene) days (Table S4).

4. Discussion

To our best knowledge, this is the first report characterizing VOC emissions from the leaves during the growth of sugarcane plants by using the GC–MS and PTR-MS analyses. The results show that VOC emission of sugarcane plants includes a total of 40 different compounds from the seven chemical classes, *i.e.,* alkanes, alkenes, aromatics, aldehydes, alcohols, ketones and terpenoids. Moreover, emission of methanol, ethanol, acetaldehyde, and to a minor degree LOX-products, monoterpenes and *m/z* 69 (not validated as isoprene) were observed by continuous PTR-MS analysis. Also, previous studies with numerous other species showed that VOC emission by plants consists not only of isoprene, but a high diversity of compounds (Kesselmeier and Staudt, 1999; Peñuelas and Llusià, 2004), and is species-specific (Tani and Kawawata, 2008; Benjamin et al., 1996). VOC emitting plant species include not only herbaceous plants (*e.g.;* (Fukui and Doskey, 2000; König et al., 1995; Kirstine et al., 1998; Winer et al., 1992)), but also trees and woody shrubs (Hu et al., 2018; Kigathi et al., 2009; Mansour et al., 2015; Zhang et al., 2015; Wiß et al., 2017). Although several VOCs observed to be emitted from sugarcane in the present study were reported in previous studies with other species (see details in Table S5), there is no report including the seven chemical compound classes identified in the current investigation. This is consistent with the assumption that still a large proportion of VOCs emitted by plants are unknown (Peñuelas and Llusià, 2004). In general, we showed that the VOCs emitted by sugarcane were belonging to the classes of non-terpenoid aliphatics, terpenoids, aromatics compounds, as well as oxygenated VOCs (OVOCs). The latter includes lipid oxidation (LOX) products.

4.1. Non-terpenoid aliphatic compounds

Among the VOCs identified, non-terpenoid aliphatic compounds (~41 %) dominated total VOC emission by sugarcane plants followed by OVOCs emission, in line with our hypothesis (i) as the OVOCs and LOX to be dominant compounds emitted by sugarcane plants. Emission of non-terpenoid aliphatics, *e.g.,* alkanes/alkenes, was commonly observed in studies with other sweet grass species, *i.e., Zea mays*, *Sorghum bicolor*, *Triticum aestivum* (Tani and Kawawata, 2008), in non-specific grasslands (Fukui and Doskey, 2000; Kirstine et al., 1998), as well as from various other herbaceous plants, shrubs and tree species (Hu et al., 2018; Mansour et al., 2015; Zhang et al., 2015; Wiß et al., 2017). (Miresmailli et al., 2013) reported the emission of a relatively large number of non-terpenoid aliphatic compounds from *Miscanthus* x *giganteus* and *Panicum virgatum*.

Microbial synthesis of non-terpenoid aliphatic compounds is well-studied (Ladygina et al., 2006) and a microbial origin of these compounds cannot be excluded from the present study. On the other hand, plant origin of biogenic emissions of $C_{6\text{-}16}$-aliphatics is supported by their frequent observation in emission studies with various tissues of different plant species. In this context, heptane as observed in emission of sugarcane of the present study was further identified as main constituent of the wood resin of two *Pinus* species (*P. jeffreyi, P. sabiniana*; (Mirov, 1961; Williams and Bannister, 1962) and balsam trees (*Bursera chemapodicta*) as well as a constituent of the essence oil of the herb *Marrubium crassidens* (Evans and Becerra, 2006; Dhifi et al., 2016; Hamedeyazdan et al., 2013). However, the synthetic pathways and functions of non-terpenoid aliphatics in plants are still largely unknown, although they are assumed to originate from fatty acid metabolism. This assumption is based on the synthesis pathways of long-chain alkanes/alkenes, which are ubiquitous in the cuticular wax layer of plants (Chikaraishi and Naraoka, 2003). Also, the synthesis of n-heptane and n-pentane emitted by sugarcane plants in the present study has been postulated to occur through branching of the main synthetic pathways of fatty acid metabolism (Sanders et al., 1975). However, information about synthesis, functioning and emission pathways of these and other non-terpenoid aliphatics in plants is scarce and needs to be elucidated in future studies.

4.2. Terpenoids

As hypothesized (i), sugarcane plants were identified as non-emitters of isoprene and moderate monoterpene emitters as also observed in other sweet grass species, *e.g., Miscanthus* (Copeland et al., 2012), maize (Wiß et al., 2017; Buttery and Ling, 1984), wheat (Winer et al., 1992; Buttery and Ling, 1984), sorghum and rice (Winer et al., 1992) in previous studies. The release of three monoterpenes (*i.e., δ*-3-Carene, p-Cymene and Bornylene), as well as the monoterpenoid compound *β*-Ionone, was observed in the present emission analyses. These compounds (*i.e., δ*-3-Carene, p-Cymene, Bornylene and *β*-Ionone) are listed as the quantitatively most important biogenic VOCs (Guenther et al., 2012) and are direct products of terpene biosynthesis or oxidative cleavage of carotenoids (Schmidt et al., 2006; Schwartz et al., 2004). In addition, the monoterpenes *δ*-3-carene and p-Cymene were emitted by sugarcane as frequently observed in the plant kingdom (Guenther et al., 1993; Geron et al., 2006), particularly for conifers (Faiola and Taipale, 2020), grass species including wheat (*Triticum aestivum*, (Winer et al., 1992), *Miscanthus* (*M x giganteus*, (Hu et al., 2018), switchgrass (*Panicum virgatum*, (Miresmailli et al., 2013), and grassland (Fukui and Doskey, 2000). Several monoterpenes/terpenoids, including the compounds of Bornylene and *β*-Ionone, emitted by sugarcane in the present study were not reported in previous investigations.

4.3. Aromatics and non-aromatic oxygenated VOCs (OVOCs)

The present results show that with a total of seven representatives, the group of aromatic compounds accounts for ~ 18 % of the total VOC emission from sugarcane plants. The emission profile included the sulfur (S)-containing compound 3-methyl-thiophene. Although the emission of S-containing aromatic compounds not been reported previously, emissions of other S-containing VOCs, including thiols, thioesters, benzothiazole, and sulfides, has been observed in emission studies with other plant species (Bestmann et al., 1997; Jardine et al., 2010). Little information is known about the synthetic pathways and possible functions of aromatic S-containing compounds. In general, the emission of aromatic VOCs has largely been ignored in previous studies. Still several herbaceous and woody plants were reported to release aromatic compounds from both, flowers and leaves, *e.g.,* tomato, sunflower, maize, Scots pine

and holm oak (Jardine et al., 2010; Zhu and Park, 2005; Coppola et al., 2017; Holzinger et al., 2001; Misztal et al., 2015). The emission of aromatic VOCs has been explicitly observed in response to various stress factors, such as heat and herbivory and was assumed to trigger protection reactions against reactive oxygen species (ROS) in plants (Kigathi et al., 2009; Misztal et al., 2015).

An unexpectedly great proportion of non-aromatic OVOCs added up to ~ 70 % of OVOCs in agreement to our hypothesis (i). Thus, it is suggested that PTR-MS instruments may be used in future studies for more reliable detection of OVOCs (Clavijo McCormick et al., 2014; Gawłowski et al., 2000; Kirstine et al., 1998). Our GC–MS analysis indicated that non-aromatic OVOCs emitted from sugarcane include a total of 12 different alcohols, aldehydes and ketones of C_5-C_{10} atoms. Moreover, the PTR-MS measurements demonstrated emission of methanol, ethanol and acetaldehyde (which are not detectable by our GC–MS method). In previous studies, the release of alcohols and carbonyls were often observed from tree and shrub species (Jardine et al., 2010; Ciccioli et al., 1993), and also from grasses (Fukui and Doskey, 2000; König et al., 1995; Kirstine et al., 1998; Buttery and Ling, 1984). The presence of great amounts of alcohols and carbonyls in essence oils and saps from various plant species (Ciccioli et al., 1993) supports the biogenic origin of these emitted VOCs. This view is also consistent with the large fraction of OVOCs emitted from sugarcane stalks (da Silva et al., 2017; Yang et al., 2013). In addition, nonanal and decanal constitute commonly emitted VOCs that also were emitted from the leaves of sugarcane plants. The biogenic origin of these compounds was strongly supported by their diurnal emission rhythm in line with our hypothesis (ii) (Owen et al., 2002). Compared to the other VOCs emitted, strong aldehyde emissions were observed in the present study with sugarcane plants. In general, the emission of volatile alcohols and carbonyls, including C_6-C_{10} aldehydes were considered as stress responses in previous studies (da Silva et al., 2017; Yang et al., 2013). However, (Cao and Hewitt, 1994) attributed aldehyde emission to reactions between ROS including adsorbents, rather than a biogenic origin. Apparently, either biosynthetic pathways or ROS activity and associated oxidation of cell material are responsible for the generation of aldehydes emitted by plants (Wildt et al., 2003).

4.4. Emissions from different developmental stages

In agreement with hypothesis (iii), VOC emissions of sugarcane plants changed ontogenetically and with season, decreasing when senescence decreased physiological activity (for terpenoids) and increasing during spring at high physiological activity. This is indicated by the particularly intense methanol emission during rapid plant growth (MacDonald and Kimmerer, 1993; Nemecek-Marshall et al., 1995; Manco et al., 2021). So far, only few studies compared VOC emissions at different developmental stages including senescence and plant ageing (Mozaffar et al., 2018; Holopainen and Gershenzon, 2010). The decrease in photosynthesis and metabolism associated with senescence may lead to reduced VOCs emission since VOC synthesis require energy that will be limited under these conditions (Holopainen and Gershenzon, 2010). In addition, stomatal conductance that can significantly influence the release of most VOCs, is significantly reduced in senescent leaves. However, the unchanged iWUE across plant developmental stages in young, mature and senescent plants, reflects the complexity of controlling factors for iWUE across plant growth/seasonal scales, which are related to the hyperbolic (*i.e.,* saturating) relationship between P_n and G_s (Stoddart and Thomas, 1982; Yi et al., 2019). Highest emission rates from young leaves compared other developmental stages are probably due to enhanced production of methanol by PME catalyzed demethylation of pectin during cell wall remodeling and formation of the homogeneous dense canopy by adult plants as reported for *Zea Mays* and grain *Sorghum* (Manco et al., 2021; Mozaffar et al., 2018). The three identified VOCs emitted by sugarcane plants at senescence included a LOX compound, which is not surprising due to the degradation of cell and organelle membranes during this developmental stage (Stoddart and Thomas, 1982; Yi et al., 2019; Thompson et al., 1997). Increased LOX activity and emission of LOX products has been found by many studies in senescent plants (*e.g.,* 117). Emission of LOX compounds from fallen leaves during drying was even higher (Karl et al., 2001). Thus, it is important to consider the developmental stage of plants (ontogenesis) for upscaling VOC emissions (Wiß et al., 2017).

4.5. Impact of VOC emission on air quality

In the present study, we show that daily total VOC emission rates of mature leaves of sugarcane are similar or even lower compared to other crop/bioenergy species, *e.g.,* 697 pmol $m^{-2}s^{-1}$ *versus* 585 (maize), 2866 (oil-seed rape), and 1766 (ryegrass) pmol $m^{-2}s^{-1}$, respectively (Havermann et al., 2022). This is also largely true for specific VOCs emitted by sugarcane; *e.g.;* for methanol with 430 pmol $m^{-2}s^{-1}$ *versus* 98.6 (maize), 2438 (oil-seed rape) and 1417 (ryegrass) pmol $m^{-2}s^{-1}$, respectively; for acetaldehyde with 172 pmol $m^{-2}s^{-1}$ *versus* 76.2 (maize), 68.9 (oil-seed rape), 158 (ryegrass) pmol $m^{-2}s^{-1}$, respectively; for LOX with 30 pmol $m^{-2}s^{-1}$ *versus* 105.4 (maize), 49.4 (oil-seed rape), and 19.6 (ryegrass) pmol $m^{-2}s^{-1}$, respectively; for ethanol with 24 pmol $m^{-2}s^{-1}$ *versus* 14.6 (maize), 58.4 (oil-seed rape), and 38.8 (ryegrass) pmol $m^{-2}s^{-1}$, respectively (Havermann et al., 2022). Since most VOCs are removed from the atmosphere by oxidation, the input quantity is a rough measure of atmospheric OH loss by VOC emission (Baly, 1935). The reaction of VOCs with atmospheric oxidants decreases the oxidation capacity of the atmosphere, thereby increasing, among other consequences, the concentration of the GHG methane, by delaying its oxidation (Atkinson, 1986). The present results indicated that most of the VOCs released from sugarcane have higher rate constants for the reaction with OH radicals than methane ($k(OH + methane) = 6.9 \times 10^{-15}$ cm^3 $molecule^{-1}s^{-1}$; (Atkinson, 1986), as also observed for the VOCs emitted from the bioenergy plant species *Salix* and *Miscanthus* (Owen et al., 2002; Hu et al., 2018; Baly, 1935). However, the total VOC emission from sugarcane was significantly lower compared to *Miscanthus* which was already 3–4-fold lower than reported for *Salix* (Owen et al., 2002; Hu et al., 2018). Thus, the VOCs emissions from sugarcane appear to be less significant for the consumption of atmospheric OH compared to other crop/bioenergy species. Also, the none of isoprene emitted indicate low OH reactivity of the VOC emissions by sugarcane, and further render this species a low-impact plant to air chemistry compared to other bioenergy crops (Jeswani et al., 2020). This finding is in contrast to our hypothesis (iv) and was also observed for ryegrass (Havermann et al., 2022). Thus, it is largely the pre- and post-harvest management that may pose negative effects of sugarcane cultivation on the atmospheric environment and human health as reported previously (as discussed in Supporting Information Text II). Monoterpene emitters such as maize, *Miscanthus* and *Salix* (Owen et al., 2002; Hu et al., 2018; Havermann et al., 2022) usually exhibit high OH reactivity due to both, high emission rates and high reactivity of isoprene and other monoterpenes with OH radicals (as evident in the rate constant of reaction of VOC with OH; k(OH + VOC)). However, a direct quantitative comparison between the results reported for different species is limited due to the use of different measuring devices, different test conditions and, in particular, the lack of quantification of some compounds released from sugarcane, as well as unrecorded emissions of short-chain C_1-C_2 OVOCs from *Miscanthus* and *Salix*.

The present results show the emission of non-terpenoid aliphatic compounds by sugarcane in addition to the OVOCs. This finding supports the view of high VOC emission diversity by sugarcane and also indicates a lack of information regarding the emission of these VOCs by other plant species thereby contributing to the uncertainties of total VOC emissions from plants. Depending on the measurement method used and the detection limits, studies are often focused prospectively on few dominant VOCs or VOC groups, *i.e.,* terpenoids, methanol and LOX products, and therefore record only part of the VOCs emitted by plants.

However, some unknown or less common VOCs also appear to be released in relatively large amounts, which could have additional impact on atmospheric chemistry and/or may have high biological significance. For instance, the group of non-terpenoid alkenes released from sugarcane exhibit particularly low-rate constants for the reaction with atmospheric OH radicals. However, compared to other well-known and dominant VOCs, information about these VOCs remains highly speculative regarding their synthesis pathways, biological functions and atmosphere impact. Still, the present results suggest that for the evaluation of the impact of VOC emissions by plants for atmospheric chemistry not only the reactivity and the emission strength of individual compounds has to be considered in future research, but also the diurnal and seasonal pattern of a broad spectrum of VOC groups, particularly for those with high OH reactivity (Wiß et al., 2017; Havermann et al., 2022).

5. Conclusions

In conclusion, to the best of our knowledge, the present work is the first to characterize VOC emissions from sugarcane leaves. Our results confirmed that sugarcane does not belong to the isoprene-emitting plant species different to other bioenergy species, *e.g.,* maize, *Salix and Miscanthus* and also the emission of other terpenoids is of less quantitative importance. Rather, the VOC emission by sugarcane plants was dominated by oxygenated compounds, for instance, oxygenated C_1-C_2 compounds, *i.e.,* methanol, acetaldehyde and ethanol, as well as LOX products. In addition, sugarcane plants also released a large number of largely unknown VOCs. This finding identifies sugarcane as a low-impact species regarding air chemistry compared to other bioenergy crops.

6. Synopsis

This research characterizes and quantifies biogenic emissions from sugarcane and indicates the relevance of this crop for regional air chemistry.

Author Contributions

Bin Hu, Jürgen Kreuzwieser, Jörg-Peter Schnitzler, and Heinz Rennenberg conceived the idea, coordinated the research, and designed the study. Mbezele Junior Yannick Ngaba, Ann-Mareike Jarosch, and Rüdiger Grote did the methodology and formal analysis. Bin Hu, Jörg-Peter Schnitzler and Heinz Rennenberg coordinated the writing of the manuscript with input from all other authors.

CRediT authorship contribution statement

Bin Hu: Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Formal analysis, Data curation. **Ann-Mareike Jarosch:** Validation, Methodology, Investigation, Formal analysis, Data curation. **Rüdiger Grote:** Writing – review & editing, Visualization, Validation, Software, Formal analysis, Data curation. **Mbezele Junior Yannick Ngaba:** Visualization. **Jörg-Peter Schnitzler:** Writing – review & editing, Writing – original draft, Supervision, Resources, Methodology, Formal analysis, Data curation, Conceptualization. **Jürgen Kreuzwieser:** Supervision, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Heinz Rennenberg:** Writing – review & editing, Writing – original draft, Supervision, Software, Project administration, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2025.109502.

Data availability

Data will be made available on request.

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