Measuring BVOC emissions released by tomato plants grown in a soilless integrated rooftop greenhouse

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A B S T R A C T

Urban design is currently promoting the inclusion of plants in buildings. However, plants emit biogenic volatile organic compounds (BVOCs), which alone or in combination with other airborne molecules such as CO_2, may result in a general increase in tropospheric pollution. Many studies have documented the effects of biotic and abiotic factors on plant BVOC responses, but few have assessed the contribution of typical CO_2 levels found in indoor work and meeting spaces. To answer this question, we monitored CO_2 and constitutive (MT-limonene) and induced (LOX-cis-3-hexenal) BVOC emissions of a fully developed tomato crop grown hydroponically inside an integrated rooftop greenhouse (i-RTG) in a Mediterranean climate. Two distinctive CO_2 assays were performed at the level of the i-RTG by supplying or not CO_2. The impact of CO_2 on plant physiological emittance was then assessed, and the resulting BVOC rates were compared with reference to EU-LCI values. MT-limonene was ubiquitous among the assays and the most abundant, while LOX-cis-3-hexenal was detected only under controlled CO_2 management. The highest levels detected were below the indicated LCIs and were approximately tenfold lower than the corresponding LCI for MT-limonene (50.88 *vs.* 5000 µg m^{-3}) and eightfold (6.63 µg m^{-3}) higher than the constitutive emission level for LOX-cis-3-hexenal. Over extended sampling (10 min) findings revealed a general emission decrease and significantly different CO_2 concentration between the assays. Despite similar decreasing rates of predicted net photosynthesis (Pn) and stomatal conductance (g$_s$) their correlation with decreasing CO_2 under uncontrolled condition indirectly suggested a negative CO_2 impact on plant emission activity. Conversely, increasing CO_2 under the controlled assay showed a positive correlation with induced emissions but not with constitutive ones. Because of significantly higher levels of relative humidity registered under the uncontrolled condition, this factor was considered to affect more than CO_2 the emission response and even its collection. This hypothesis was supported by literature findings and attributed to a common issue related with the sampling in static enclosure. Hence, we suggested a careful monitoring of the sampling conditions or further improvements to avoid bias and underestimation of actual emissions. Based on the main outcomes, we observed no evidence of a hazardous effect of registered CO_2 rates on the BVOC emissions of tomato plant. Furthermore, because of the low BVOC levels measured in the i-RTG, we assumed as safe the recirculation of this air along building's indoor environments.

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1. Introduction

Worldwide climate emergencies and intense gentrification are forcing the scientific community and citizens to enact timely actions for the containment of forecasted environmental and socioeconomical contingencies [1]. Among the effective strategies recommended, the systematic expansion of green infrastructures in urban centres has been encouraged, particularly by European councils and local neighbourhoods [2,3], to solve issues related to food accessibility and social exclusion [4–6] as well as to tropospheric contamination [7–9]. The environmental performance of existing buildings can be improved by integrating plants inside and outside of them [10], not necessarily by means of high-cost technologies. Innovative systems, such as integrated rooftop greenhouses (i-RTGs) [11–13], have demonstrated the multiple benefits provided in terms of energy use efficiency [12], carbon emissions reduction [14], and energy and food production [15,16].

The benefits associated with plant removal capacity of air contaminants have been widely reviewed in the green retrofitting literature [7,17–20]. However, this capacity seemed to be overestimated with respect to the measured removal efficiency [21–23] due to species-specific plant mechanisms and to the same environment considerably affecting plant response in terms of indoor and outdoor air recovery [17,21,24]. In the wild, plants can release [25,26] tons of biogenic volatile organic compounds (BVOCs) annually into the atmosphere during photosynthetic activity [27–29], which have also been detected in urban areas [30,31] and domestic spaces [23,32,33]. The ultimate impact of BVOCs on indoor air quality is still uncertain [17,32,34], although because of the high concentration and chemical reactivity, potential harm to human health has been warned [35–37]. For some BVOCs, concern levels were assessed and included along with those of other volatiles in the EU-LCI tables for enclosed spaces [38,39]. Depending on indoor conditions, the composition and amount of BVOC emissions change and can increase considerably, as observed under elevated ozone [37,40] and temperature [25,41] levels. Emission blend mutations have been referred to as a substantial adaptation of plants to the presented environment [42,43] and were demonstrated to follow typical patterns. Without stimuli, either biotic or abiotic, plants emit constitutive BVOCs, mainly mono- and sesquiterpenes, regulated by the temperature–light gradient [25,44,45]. Under non-physiological conditions, commonly during a stress event (e.g., drought and insect plague), plants emit predominantly volatile derivates of the lipoxygenase pathway [25,46].

Among the stress factors affecting BVOC emissions, the implication of CO_2 has also been studied [47,48] given the higher levels recorded currently than in the past 30 years and those foreseen [49]. Although there is still uncertainty about the effect of CO_2 at both ambient and elevated concentrations, a trend toward reduced plant response under elevated CO_2 has been documented [50–52], although it is connected to the length of exposure. More specifically, this has mainly been detected at short-term exposure. Longer term exposure was believed to result in plant adaptation with almost no consequences on total emission release [48,53]. Additionally, combining high CO_2 with increasing temperature and other common stresses, such as drought, was shown in the short term to have a contrasting effect to the inhibiting effect of CO_2, favouring plant emission activity [54–56]. In a recent study [57], different CO_2 regimes were applied for a short time, individually or in combination with defined temperature rates, to the leafy species *Artemisia annua* L. The results demonstrated that a decreasing effect on total emissions was significant only when the plant was exposed to both elevated CO_2 (800 ppm) and temperature (>30 °C); this also confirmed the predominant effect of temperature on the induction of plant emissions. However, high variability and different outcomes were also noted depending on different factors, for instance, the sampling condition (field or laboratory study), the plant status and the species [51,58].

Among indoor crops, tomato (*Solanum lycopersicum* L.) is one of the top crops because of its remarkable nutritional and commercial aspects [59–61]. Regarding the volatile profile, tomato plants have been investigated under conventional and stressed conditions to determine BVOC variations between constitutive and induced emissions [62,63]. Among the wide range of BVOC classes, terpene components are usually detected in physiological emission blends [64,65]. Monoterpene and sesquiterpene release via plant photosynthesis was reported under a positive temperature gradient sustained over time [64,66]. Despite the ubiquity of terpene [67], induced emissions from tomato may change substantially according to elicitation and intensity subordination [63]. Lipoxygenase derivates were the volatiles most documented under extreme temperature rates [62], ozone fumigation [68], insect wounding [69], and combined biotic and abiotic stresses [70,71]. To the best of our knowledge, potential variations in tomato emissions associated with different CO_2 levels have not been reported, since related measurements were conducted at ambient CO_2 levels only.

Compared to most horticultural species, tomato plants account for a considerable emitting surface, and therefore, BVOC amounts eventually reach levels of attention over prolonged exposure [72]. Few studies have been conducted on the assessment of tomato emissions into the environment [66,73–75]. Among these, their association with CO_2 was briefly mentioned [66]. Additionally, in an i-RTG on the ICTA building on the Universitat Autònoma de Barcelona campus, the emissions from a leafy plant (*Phaseolus vulgaris* L.) were previously investigated through a static chamber under ambient conditions by checking temperature, light and relative humidity parameters (with the exception of CO_2), and emission rates below the advised EU-LCI [76] were found. Emissions from larger plants (e. g., tomato), which in southeast-oriented i-RTGs [77] are cultivated annually, have not yet been studied. Compared to a controlled greenhouse [66,70,73,74] and although frequently adjusted to crop requirements, climatic conditions in i-RTGs are much more variable due to the top location, which enhances exchanges with the surroundings. Additionally, according to the building's recirculation system, air coming from the greenhouse floor could be efficiently exploited to warm up the lower space, increasing the living quality of indoor environments, such as offices [12]. Therefore, in this study, in addition to measuring tomato plant emissions, the contribution of CO_2 was also analysed. This was performed under two sampling conditions in a static chamber, one at the CO_2 concentration generated by the enclosure and one at a controlled concentration maintained at the ambient (i-RTG) levels. The research questions investigated were as follows:

- Are the BVOC emissions of tomato plants grown under i-RTG conditions below the reference EU-LCI values to be safely recirculated to indoor spaces?
- Does CO_2 control significantly affect constitutive BVOC emissions during sampling?
- If so, do emissions increase or decrease under uncontrolled CO_2?

2. Materials and methods

2.1. Experimental conditions

The study was conducted in two consecutive warm seasons (spring-summer), with one experiment conducted in 2021 and the following in 2022. Plant cultivation and experimental setup were carried out hydroponically in the abovementioned i-RTG (Fig. 1A.2). In both campaigns, *Solanum lycopersicum* cv. Arawak was grown in the greenhouse and intercropped with another cultivar, cv. Siranzo in 2021 and Rosa de Cadiz in 2022. Cultivars Siranzo and Arawak were chosen for the volatile profile investigation in 2021 and 2022, respectively. Despite slight morphological differences, the emission blend composition of the plants was assumed to be similar and consistent with previous studies (see Table S1 in the Supplementary Materials). In both cases, the hydroponic system consisted of 12 parallel rows of perlite substrate bags (40 L) where plants were distributed equally along the row (0.30 m) and between the rows (0.80 m) (Fig. 1A.1), providing a density of 3 plants per m^2 and a total cultivated area equal to 41.8 m^2 in 2021 and 27.8 m^2 in 2022. In the two years, the crop cycle in the i-RTG had an equivalent duration of approximately 5 months (135 days). The duration of the cycle was defined as days after transplanting (DAT), which occurred in mid-March, and it finished at the end of July.

Cultivation parameters were checked continuously and adjusted when necessary to maintain adequate and stable growing conditions over the season. This included daily measurements of the pH and electrical conductivity (EC) of water tanks, dripped solution and leachates, as well as of environmental temperature, relative humidity, and radiation (CS215 system, Campbell Scientific and L202, Hukseflux). Ambient CO_2 was periodically measured in the greenhouse space with a portable gas analyser (U-CO_2-915, GLA132 Series, LGR) to provide updated ambient levels. The internal conditions of the i-RTG were managed by a remote station (Siemens Building Technologies Ltd) that regulated the opening of the surrounding façade to dissipate the passive heat collected from the building.

Plant development was monitored weekly based on morphological traits by measuring stem height and leaf area, counting the blossoms, and weighing the biomass collected from the pruning and harvested fruits. Additionally, over the whole cultivation cycle of each season, the heating degree days (HDDs) inside the i-RTG were calculated by applying Equation [1] of Ref. [78]. The single HDD was derived from the average of the maximum and the minimum temperature (T_{max}, T_{min}) and the lowest temperature at which tomato can thrive (T_{base}), which was fixed at 10 °C. This value provided the minimum temperature required for the plant's metabolic activity. This information was then used as a direct and indirect measurement of plant growth in the i-RTG to determine crop resemblance and diversity among the two cultivation seasons.

$$HDD = \frac{(T_{max} + T_{min})}{2} - T_{base}$$ [1]

2.2. Volatile monitoring and CO_2 management

BVOC investigation was conducted on mature plants at first fruit ripening (82 DAT) over the whole productive stage. Emissions were concentrated in a static enclosure and trapped dynamically onto Anasorb tubes (CSC, 6 × 70 mm–100/50 mg, SKC) at 250 mL min^{-1} constant flow using the sampling settings reported in a previous study for the determination of green bean emissions [76]. The aerial part of one tomato plant was gently enclosed in a suspended LDPE cylindrical chamber (1.16 m diameter × 2.23 m height) to avoid mechanical injury and minimize the load of the plastic wall around the plant (Fig. 2A.2). In our study, we investigated the emission response to CO_2 variation because of the static enclosure. First, the inertia of the static enclosure was determined by measuring radiation (Rs), temperature (T), relative humidity (RH), and CO_2 fluctuation in the empty chamber over different time intervals (5–60 min). Then, the variation in CO_2 before and during plant enclosure was recorded every minute with the portable gas

Fig. 1. Crop distribution in the i-RTG in the early growing stage (A.1) and a panoramic view from the building's atrium of mature tomato plants in the i-RTG (A.2). Both pictures were taken in the 2021 season.

analyser. After 5 min of closure, a progressive drop in CO_2 relative to the starting concentration was observed. Therefore, short consecutive samplings of 5 (1.25 L) and 10 (2.50 L) minutes were carried out to contain alterations in constitutive plant emissions under uncontrolled CO_2 (=unadministered CO_2). Feedback on plant physiological performance was derived from 1-min records of Rs, T, RH, and CO_2 (Fig. 2A.1). In addition, plant photosynthetic rate (Pn) and stomatal conductance (g_s) were estimated based on the empirical formulas of Ref. [79,80], respectively, in absence of measuring tools. Missing input data for the calculation of g_s were retrieved from comprehensive literature [81] based on C3 plants. The results obtained in 2021 were compared with an equivalent trial performed the following season (2022). Air samples were instead collected at CO_2 levels equivalent to the ambient, achieved by controlled CO_2 purge (≥99% purity) into the chamber throughout the length of sampling (=administered CO_2). Sampling was usually carried out between 10:00 a.m. and 1:00 p.m. (CET) because most of the greenhouse tasks were performed in the morning, and this time was thus considered the longest period of exposure to plant emissions. Throughout the season, volatile collection was repeated to provide replicates for the statistical analysis. Blank samples from a pure air tank were generated as benchmarks for all samples collected.

2.3. Determination of selected BVOCs in the sampled emissions

Only two elective volatiles were analysed in the total emissions sampled that represented specific BVOC classes of constitutive and induced tomato plant emissions (see Table S1 in the Supplementary Materials): limonene for the monoterpenes (MT) and *cis*-3-hexenal for the lipoxygenase derivatives (LOX).

Quantitation of BVOCs was performed following the NIOSH protocol [82] BVOCs trapped in Anasorb tubes were extracted with 1 mL of liquid carbon disulfide (CS_2 for spectroscopy, ≥99.9%, Thermo Scientific) collected in 1.5-mL vials. Samples from 2021 were analysed using a Thermo GC−MS system (GC: TRACE 1300/1310, MS: ISQ7000, Thermo Scientific, USA) using the working conditions described elsewhere [76]. Samples obtained in 2022 were analysed using an Agilent GC−MS system (Agilent 7890A GC coupled to a 5975C MS). Calibration with external standard solutions ensured data comparability between both instruments. The instrumental conditions were maintained constant among instruments. Extract volumes of 2 μL were injected in splitless mode (1 min, 240 °C), and BVOCs were separated using a TG-WAXMS capillary column (TraceGOLD™, 30 m × 0.32 mm × 1 μm, Thermo Scientific, USA) with a constant helium flow (3 mL min^{-1}). The GC oven programming consisted of an initial temperature step at 35 °C (held for 2 min), followed by a 10 °C min^{-1} gradient up to 215 °C (maintained for 4 min). The MS transfer line temperature was set at 250 °C, and the ion source was heated at 150 °C with 70 eV as the ionization potential. Data acquisition was performed in SIM mode to optimize instrumental sensitivity and reproducibility. Data processing and BVOC quantitation were performed with either MassHunter Workstation 10.1 (Agilent GC/MS data) or Chromeleon Software (Thermo GC/MS data). Compound identification and quantitation were performed by comparison of peak retention times and peak areas with external standard solutions as described elsewhere [76].

In this study, the instrumental lower limit of quantitation (LLOQ) corresponds to the concentration value that can be quantified with a relative standard deviation (RSD%) ≤ 21% upon consecutive analysis (See Table S2 in the Supplementary Materials). The instrumental dynamic range was typically between 10 and 100 ng mL^{-1}.

The calculation of the BVOC emission rate (ER_{BVOC}) was based on the canonical Equation [2] for the determination of the emission rate of a volatile. This is the difference between the products of the volatile emitted by the plant ($BVOC_p$, μg m^{-3}) in the sampled volume (V_c, m^3) and its amount found in a blank sample (either in the empty chamber or in scrubbed air, $BVOC_c$) divided by the product between the sampling time (h, hr) and either the fresh weight (gfw, g) of the leaves or of the total biomass (stem + leaves + fruits) enclosed, or the projected leaf area (m^2). In the results section, this is referred to as the weight of fresh leaves.
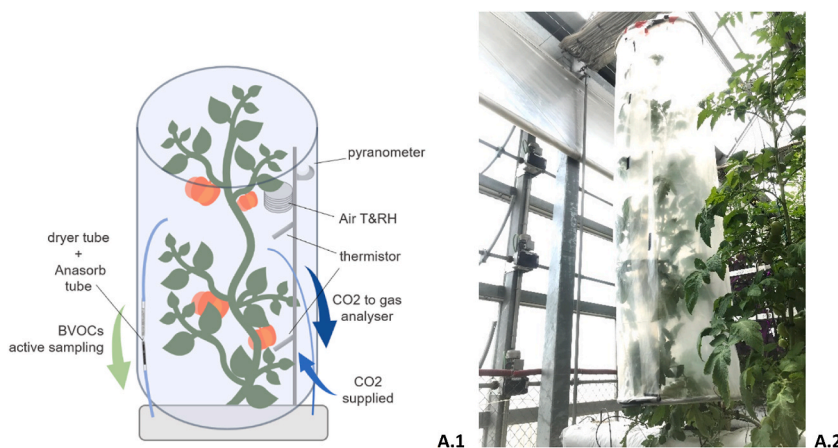

Fig. 2. Simplified representation of the dynamic (active) emission sampling with static enclosure, with or without CO_2 supply (A.1). Picture taken during the setup of the sampling chamber on a tomato plant (A.2).

$$ER_{BVOC} = \frac{(BVOC_p \times V_c) - (BVOC_c \times V_c)}{gfw \times h}$$ [2]

2.4. Statistical analysis and variable impact calculation

Individual BVOC emissions were compared between the sampling intervals (5 and 10 min) within the same CO_2 conditions (administered or unadministered) and between the CO_2 conditions within the sampling intervals using the Wilcox test (paired or unpaired). Dependencies and independencies between the variation rates of monitored and predicted variables (Rs, T, RH, and CO_2 concentration) were also compared using linear regression models and ANOVA tests (type II). The relationships between the sampled BVOC emissions at the 5- and 10-min intervals of each CO_2 assay and the considered variables were preliminarily assessed through principal component analysis (PCA). Finally, the variation rates of both emissions and variables were log-transformed before their computation in paired plot matrices for the determination of the correlation coefficient (R^2). Differences were assigned as significant at a probability value $p \leq 0.05$, and correlations were considered meaningful at a R^2 coefficient comprised between ± 0.50 and ± 1 and significant at a probability value $p \leq 0.05$. All tests were performed with R software (version 4.2.2).

3. Results

3.1. Crop heat accumulation and growth during the two cultivation seasons

The sum of the heating degree days (HDDs) calculated from the DAT in the i-RTG until the last sampling day for each of the two experimental seasons (see Fig. S1 in Supplementary Materials) was significantly higher (p = 0.001) in 2021 (3039.82) than in 2022
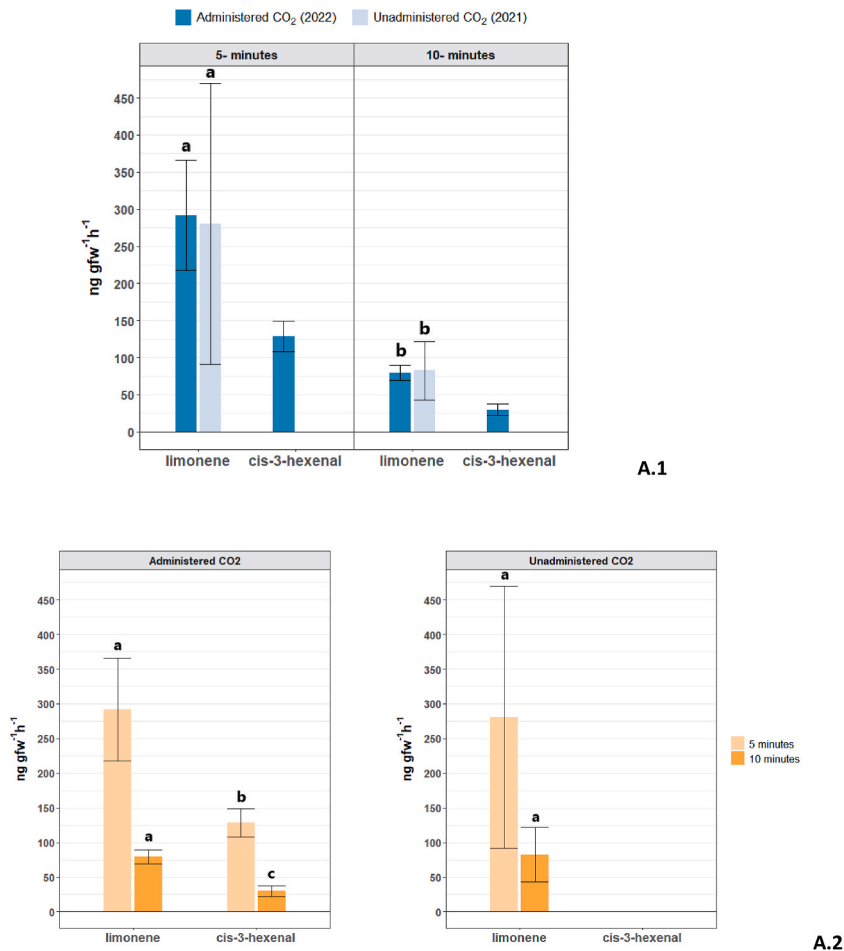

Fig. 3. Average $\pm$ SEM (n = 9, 2021; n = 5, 2022) ERs of the monoterpene (limonene) and lipoxygenase derivative (*cis*-3-hexenal) detected in the static enclosure containing one mature plant at 5- and 10-min sampling intervals under different CO_2 assays. Different lowercase letters indicate significantly different emissions (p $\leq$ 0.05); average ERs of the single volatile are compared between the CO_2 assays within the same sampling interval (A.1) or between the sampling intervals within the same CO_2 assay (A.2).

(2323.41). In detail, comparing the maximum and minimum T rates of the two periods, there was a significant difference (p = 0.001) between the T_{max} average of 2022 (37.12 °C) and 2021 (32.81 °C). In fact, BVOC collection in 2022 covered approximately one week less than in 2021, and it was concluded 21 days before the last day of sampling in 2021. Considering plant morphological development over the growing cycles (see Table S3 in the Supplementary Materials), the mean total fresh biomass (stem + leaves + fruits) measured
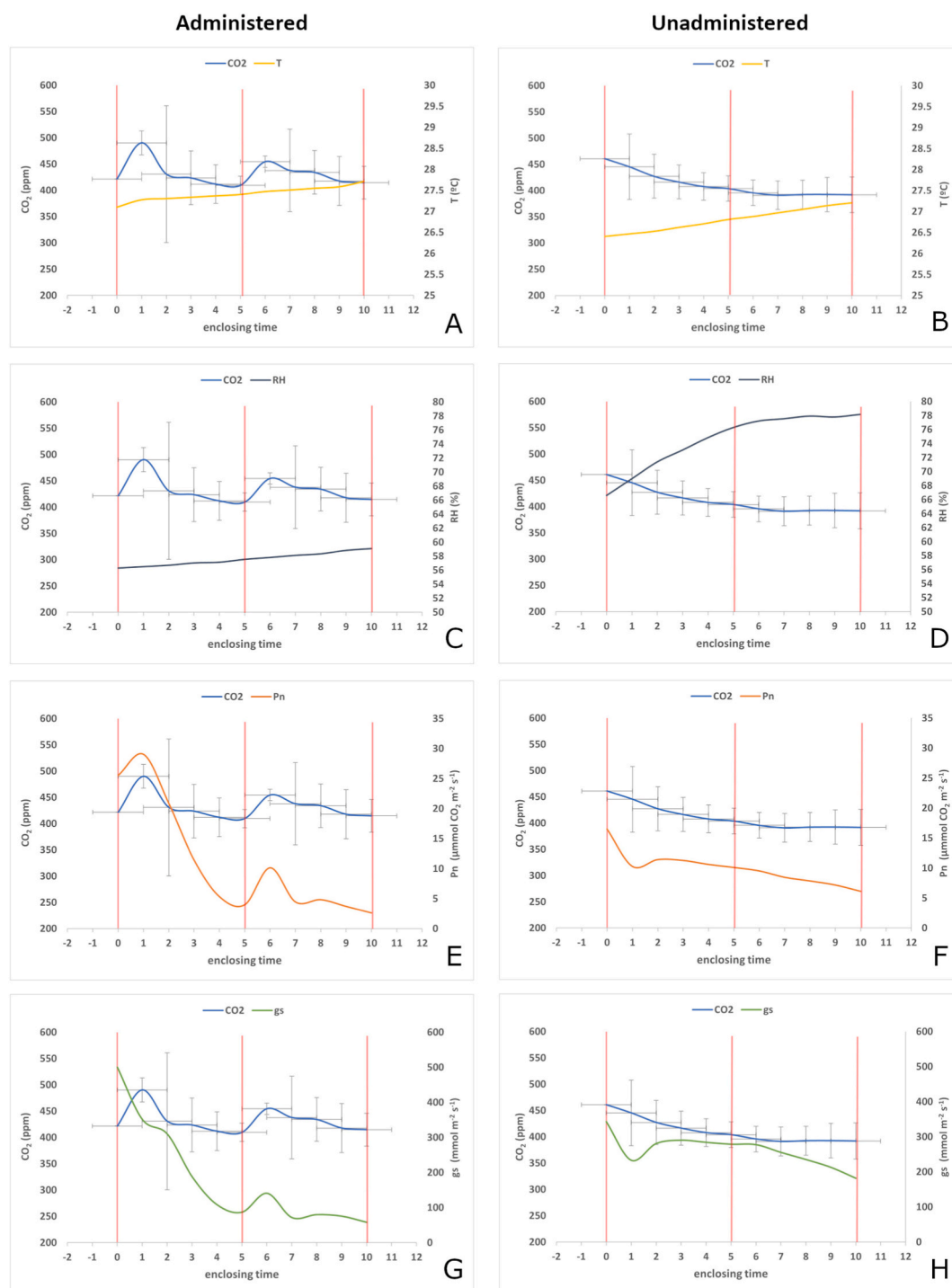

Fig. 4. Mean ± SD of CO_2 levels interpolated with the monitored environmental variables (T: 'A' and 'B'; RH: 'C' and 'D') and predicted physiological ones (Pn: 'E' and 'F'; g_s: 'G' and 'H') under administered (left) and unadministered (right) CO_2 condition along plant enclosure sampling. Red bars delimit the principal sampling intervals considered (5- and 10- minutes).

in 2021 was significantly higher (4.23 kg, p = 0.007) than that measured in 2022 (3.08 kg). However, comparing individual organ weights, the overall difference was provided only by the mean weight of fruits (p = 0.002), rather than that of leaves or stem.

3.2. BVOC emission rates and amounts in the i-RTG with respect to indoor LCI values

Average emission rates (ERs) for the two volatiles at both the 5- and 10-min sampling intervals under the two different CO_2 assays are reported in Fig. 3 and summarized in Table S6 of the Supplementary Materials.

During the two experimental seasons, MT-limonene was usually detected under both the administered and unadministered CO_2 assays, while LOX-cis-3-hexenal was detected only under administered CO_2 (Fig. 3A.1). The emissions of both volatiles were higher in the first 5 min than in the following 10. Between short and long sampling intervals there was no significant difference in the levels of limonene (p > 0.1) in either of the two CO_2 assays, whereas a significant difference was observed in those of *cis*-3-hexenal (p = 0.002) (Fig. 3A.2). Overall, Limonene emissions were substantially higher but not significantly different under the administered assay (Fig. 3A.1). Moreover, under the same condition, MT emissions were on average the most abundant in both the 5- and 10-min samples, accounting for 65.2% and 72.8%, respectively, compared to LOX emissions, which accounted for 34.8% and 27.2%, respectively. Likewise, the average minimum and maximum percentages collected during 5 and 10 min were 44.4–78.9% and 50–87.2% for limonene and 21–55.6% and 12.8–50% for *cis*-3-hexenal, respectively. Considering the calculated ERs (Table S6), for the constitutive MT, the highest amount was reported under unadministered CO_2 (1752.19 ng g^{-1} h^{-1}), while for the induced LOX, it was reported under the administered assay (181.8 ng g^{-1} h^{-1}).

3.3. Enclosure performance prior to emission sampling

The tested inertia of the empty chamber provided no significant variation in the measured Rs, T, RH, and CO_2 concentration during the whole enclosure time (up to 60 min). Radiation inside and outside the chamber did not vary significantly. Over the whole cycle, Rs recorded at the crop level (see Table S4.1 in the Supplementary Materials) was approximately 29% (2021) and 48% (2022) of the total Rs measured 2 m above the canopy, which was far below the standard illumination supplied in other greenhouses [57,74,83]. However, according to previous assessments performed on this i-RTG [84], such rates were still consistent with those found in common greenhouses and would ensure plant photosynthetic activity. Therefore, the effect of radiation on CO_2 assimilation was not contemplated henceforth.

3.4. Comparison of environmental and physiological trends across different CO_2 assays

Across the CO_2 assays, between 5- and 10-min sampling intervals no significant differences (p > 0.1) were highlighted in the mean values (Table S4) of both the monitored and predicted variables. However, between the assays significantly higher levels of RH and g_s under the unadministered condition were observed at both 5- (+16%, p = 0.04) and 10- (+18%, p = 0.02) minutes sampling for RH, at 10 min only (+124 mmol m^{-2} s^{-1}, p = 0.02) for g_s. Fig. 4 reports variables performance in relation to the CO_2 tendency during the enclosing time. According to the mean values registered, with respect to the i-RTG concentration by the end of the first and the second sampling term CO_2 decreased up to 14 and 30 ppm under the unadministered condition and increased up to 8 and 11 ppm under the administered one. However, according to the variation rates, a general CO_2 drop was always observed within the first 5 min of enclosure across both the assays. Although the decrease was higher under unadministered (−57.01 ppm) than under unadministered (−17.60 ppm) CO_2 it was not statistically significant (p = 0.24). However, on the overall 10 min CO_2 decrease under the first condition (−69.04 ppm) was then significantly higher (p = 0.042) than under the second one (−11.22 ppm) where partial recovery of CO_2 (+6.38 ppm) occurred. Considering T and RH, throughout the sampling a progressive increase was registered under both CO_2 assays (Fig. 4A and B; C and D), with overall higher RH increase (±18%) than T one (±1.50 °C). Despite slightly higher rates observed under the unadministered (0.40–0.80 °C; 9.70–11.57%) than under the administered condition (0.23–0.41 °C; 2.15–3.64%) no significant differences (p > 0.05) were individuated. Consistent with CO_2 trend, also predicted Pn and g_s were found to decrease along the sampling (Fig. 4E and F; G and H). Within the individual assay substantial Pn and g_s decrease was higher under administered CO_2 (−21.53–22.91 µmol CO_2 m^{-2} s^{-1} and −413–442.72 mmol m^{-2} s^{-1}) rather than the unadministered condition (−6.40–10.38 µmol CO_2 m^{-2} s^{-1} and −64.39–161.41 mmol m^{-2} s^{-1}). However, their variation rates of between the assays were not significantly different.

3.5. Implication of the CO_2 assay on plant emissions and the enclosing conditions

Exploratory principal component analysis (PCA) scores and data distribution (see Fig. S2 and Table S5 in the Supplementary Materials) revealed that emissions collected under administered CO_2 were primarily related to environmental factors, especially those sampled within the 5-min interval and mostly for the LOX volatile. Temperature and CO_2 emerged as the main relevant variables, while Pn, g_s, and RH in this order showed less influence. Conversely, the data suggested little to no relationship between environmental and physiological factors and MT emissions.

Correlations between the five variables monitored and predicted are shown in Fig. S3 of the Supplementary Materials. Between constitutive and induced emissions there were no relationships ($R^2 \leq 0.40$) under any of the CO_2 assays. Between the emissions and the five variables, there were correlations only under administered CO_2. There were negative correlations between MT emission and increasing T ($R^2 = -0.60$) and RH ($R^2 = -0.50$), respectively in the first and in the second sampling interval. There was a positive correlation between LOX emission and decreasing CO_2 ($R^2 = 0.60$) in the second interval only. Among the variables several

correlations were additionally individuated (Fig. S3). Within the 5 and the total 10 min of sampling T and RH were significantly positively correlated ($R^2 = 0.67$ and 0.73, $p \leq 0.01$) and mutually explained their increasing rate ($p = 0.03$ and $p = 0.01$) under unadministered CO_2, whereas this was not found under the administered condition. The variation of CO_2 appeared to be uncorrelated with T and RH in any of the two cases. However, significant positive correlations with CO_2 were found under unadministered CO_2 for the whole enclosure time with Pn ($R^2 = 0.78$ and 0.73, $p \leq 0.01$) and g_s ($R^2 = 0.58$ and 0.68, $p \leq 0.05$ and 0.01). Decreasing CO_2 levels also explained significantly ($p \leq 0.01$ and 0.05) and partially significantly ($p \leq 0.03$ and $p = 0.07$) both Pn and g_s variations, respectively. These correlations were however not highlighted under administered CO_2, where instead both Pn and gs were correlated with T in the first sampling term and with RH in both the terms. The relationship was negative ($R^2 = -0.70$) with the first but positive ($R^2 = 0.5$ and 0.90, $p \leq 0.01$) with the second. In contrast to CO_2 in the unadministered assay, in this case none of the variables explained ($p \geq 0.05$) the variation rates of the physiological variables.

4. Discussion

4.1. Effects of CO_2 conditions on plant emissions during the two sampling intervals

The aim of this study was to assess tomato plant emissions in an i-RTG and compare them to existing LCI values and levels found in previous assessments to evaluate the potential harm to human health in the i-RTG and in the offices where this air could be recirculated. Short sampling intervals of 5 and 10 min were used to investigate the impact of CO_2, comparing two sampling conditions: controlled (=administered) and uncontrolled (=unadministered) environmental CO_2 levels. The study also measured HDDs as a function of plant development during each separate season, which significantly differed only in terms of average T_{max} that was higher during the experiment performed with the administration of CO_2. However, the weight of traditional emitting biomass (leaves and stem), excepting the fruits, remained similar throughout the cycles. These preliminary outcomes suggested that investigated crops were rather similar, therefore emission variations were researched in the corresponding sampling conditions.

Similar MT-limonene emissions were found across the different CO_2 assays. However, administration of CO_2 affected the detection of LOX-cis-3-hexenal volatiles, with significant differences observed between the two intervals. Overall, average emissions were higher in 5-min samples and under administered CO_2. The most abundant and ubiquitous volatile was MT-limonene. Nevertheless, the highest emission recorded in the i-RTG (50.88 µg m^{-3}) over the 2021 season was approximately tenfold lower than the corresponding EU-LCI (5000 µg m^{-3}). Likewise, the highest LOX emission was at least eightfold lower (6.63 µg m^{-3}) than that of the MT. Comparing these levels with resembling studies on tomato emission assessment in greenhouse environments [66,73], there were some consistencies. In our i-RTG limonene and *cis*-3-hexenal levels were comprised between 0.01–9.13 and 0.27–1.65 ppb, respectively, which fell within the intervals found by Ref. [73] under normal or stressed conditions (0.035–40.4 ppb for MTs and 0–20 ppb for LOX volatiles). Under similar experimental conditions (open bottom chamber and similar inner CO_2 trends), Ref. [66] retrieved for terpenes and LOX derivatives emission indices (EIs) at steady and stressed condition. Higher EI (>3) was reported for terpenes than for LOX compounds in the first condition, then much lower EI (<2) for the first ones was measured than the second ones (EI > 6) during the stress occurrence. In contrast to these results equivalent limonene and *cis*-3-hexenal EIs measured under our CO_2 assays were substantially similar (<3).

Typically, emissions of MTs are observed to increase in response to a quasilinear temperature gradient [46,85] within a tolerant range for the plants before experiencing structural damages which may affect the normal emission activity. However, studies have reported emission disruptions due to occasional or prolonged temperature increases [86].

With respect to CO_2, the relatively few studies conducted on the emission responses at determined CO_2 concentrations provided conflicting or not fully consistent results [48]. Physiological MT emission is generally slowed by increasing CO_2, as terpene production implies the activation of the same enzymatic system involved in the transportation of O_2 during photosynthesis [42,46,86–88]. However, it was generally observed that supplying CO_2 up to normal ambient concentrations (~400 ppm) did not have a relevant impact on MTs and overall emission feedback unless temperature rose without exceeding damage thresholds (over 35 °C and up to 47 °C) [54–57]. In contrast, applying high CO_2 concentrations (>800 ppm) at high T would decrease overall emissions [56,57,86].

In our case, under administered CO_2 flush within the first 5 min, the relationship between the positive T gradient and limonene emissions was found to be unexpectedly negative, and no relationship at all was found with increasing RH or with (decreasing) CO_2 levels. Conversely, despite CO_2 decrease, ERs were still slightly higher within 5 min than after CO_2 stabilization achieved after until the end of sampling. In this second interval, MT were instead negatively correlated with the increasing RH rather than with T and still uncorrelated with CO_2. Under unadministered CO_2, no relationship was found with the constitutive emissions, but negative correlation between T and RH was maintained throughout the sampling, as well as the positive correlation between overall decreasing CO_2, Pn and g_s. . Based on these outcomes, it could be rationally assumed that T and RH had a relevant implication on the MT emission response when no administration is applied. The increase of RH has been traditionally associated with a common issue individuated during volatile sampling in static enclosures. As reported by experimental tests [89–91], within a relatively short timeframe (3 min), despite preconditioning and thorough sampling, humidity levels can increase quickly due to instant plant transpiration substantially affecting both the plant's regular emittance and the goodness of the emission sampled [89–91]. This condition would be confirmed in our study by the tight correlations found between physiological Pn and g_s and the CO_2 variation that even explained the two variables. On the other hand, under the administered condition the highest T and RH registered (T_{max} = 32 °C, RH_{max} 60%) were much below extreme levels reported, plus no correlation was found between CO_2 rates and the physiological response (Pn and g_s decrease). This suggested that supplying CO_2 up to fixed environmental levels perhaps mitigates the quenching action of RH on plant emission release and sampling bias. However, beyond 5 min, sampling constitutive emissions can be tricky making the sample less reliable due to the loss of stable conditions inside the static enclosure.

LOX emissions have been extensively investigated in field studies, and they have been found to be rapidly released following an abiotic or biotic stress event, usually associated with mechanical injury of the cellular structure. Instead, MT emissions are mostly subordinated to T under a characteristic slow and extended release [43,88,92–95]. Currently, the relationship between LOX emissions and the variation of CO_2 is unclear, mainly due to the few investigations on this topic. So far, there was no evidence of a correlation between high CO_2 levels (720 μmol mol^{-1}) and these volatiles in comparison with environmental CO_2 concentration did not proved. Furthermore, even the combination of a mechanical stressor (insect chewing) with each of these two conditions (high and ambient CO_2 levels), missed this correlation [93,96]. It was also unclear the positive feedback of combined increasing T (below stress thresholds) and ambient CO_2 levels, though hypothesis was scarcely supported due to the lower correlation between LOX volatiles and T compared to the MTs [67,92]. There were exceptions, such as in the case of tomato, where Ref. [62] found direct correlation with the increase of LOX emission and T under normal CO_2 concentration starting from chilling and heating degrees (−7 °C and 49 °C) because of a breakage in the cell membrane. However, further field studies [67,71] found out that stress-induced LOX emissions were quite common and independent of temperature increases.

In the case study, under administered CO_2, the significantly higher rates of LOX emissions collected in the short sampling interval were strongly correlated with the initial CO_2 drop and still correlated when restoration of pre-sampling levels was achieved (10 min). Conversely, it should be noted that without CO_2 supply, emissions were not detected. It is important to consider that the occurrence or absence of LOX compounds is likely due to a stress event, which may include a combination of environmental factors such as temperature, humidity, and CO_2 concentration. In the case of tomato plants, the connection between these volatiles and the type of elicitor [67,69,71,83] and the role of the LOX kinetic response in the expression and the total amount of volatile released has been demonstrated [97]. Therefore based on the reviewed literature, the inverse correlation between progressive CO_2 decrease plus significantly higher RH rates and LOX emissions could be hypothesized even if it was not determined. Conversely, MTs were generally found to be the most abundant and far ubiquitous under multiple stress conditions [64,67,73,83]. According to these findings and given the much higher gradient of RH (up to 71.9% at min 5 and up to 79.4% at min 10) under uncontrolled rather than controlled CO_2 assays, humidity could again be considered the determining factor in the fulfilment of LOX-cis-3-hexenal collection. Eventually, RH may also be determined as the driving factor in the modulation of the stress response in plants.

5. Conclusions

In this study, it was observed that BVOC emissions generally decreased over extended sampling under both unadministered and administered CO_2. Similar variations of Pn and g_s observed between the two assays suggested a similar physiological performance under the different CO_2 conditions. However, in the unadministered assay the progressive decrease of CO_2 appeared to be tightly connected with the decrease of both the physiological variables. Even if no relationships were found between constitutive nor induced BVOCs and the variation of these variables (Pn, g_s, and CO_2) lower emissions collected under this condition suggested, indirectly, the impact of low CO_2 concentration on overall plant emission activity. On the other hand, in the administered assay positive correlations individuated among increasing CO_2 and LOX emissions also suggested the implication of this variable on the release of induced emissions. Conversely, the absence of correlations with MTs made difficult to assess the actual impact of CO_2 on constitutive emissions.

Furthermore, it has been observed a significant implication of the increase of relative humidity on both MT and LOX emissions under unadministered condition that was likely to be connected to the sampling set up, as demonstrated in the literature. Instead, this effect was not fully individuated under administered condition where indeed lower RH levels were observed and that were positively correlated with plant physiological response.

It could be reasonably assumed but not confirmed, then, that under administered condition CO_2 supply partially contributed on plant BVOCs emission, whereas under unadministered condition its contribution remained unclear and was rather prevailed by relative humidity factor. To fill this gap, altogether proper adjustments of the sampling setting and accurate monitoring of all the variables involved may improve the performance of static sampling and reduce technical issues responsible of errors and incorrect BVOCs estimation.

Overall, monoterpene and lipoxygenase derivatives emissions released by tomato plants in an i-RTG at environmental conditions (temperature, relative humidity, radiation, and CO_2) are expected to be safe over longer periods of exposure. However, it should be noted that further research would be needed to confirm measured BVOC levels since for many of them referencing EU-LCI values are currently still missing (e.g., LOX derivatives). In addition, based on the configuration of the building, designed air recirculation in the closed spaces of the lower floors for energy and quality purposes is likely to be implemented in the future without bringing about dangerous conditions for human health.

Data availability statement

Data are included in the article and in the supplementary material referenced. Additional data will be made available on request.

CRediT authorship contribution statement

Gaia Stringari: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Joan Villanueva:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Data curation. **Elisa Appolloni:** Writing – review & editing, Investigation. **Francesco Orsini:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Gara Villalba:** Writing – review & editing,

Supervision, Resources, Conceptualization. **Xavier Gabarrell Durany:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e23854.

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