Atmos. Meas. Tech. Discuss., 8, 11779–11816, 2015
www.atmos-meas-tech-discuss.net/8/11779/2015/
doi:10.5194/amtd-8-11779-2015

Atmospheric Measurement Techniques
Open Access
Discussions

A new plant chamber facility PLUS coupled to the atmospheric simulation chamber SAPHIR

T. Hohaus[1,*], U. Kuhn[1,a,*], S. Andres[1], M. Kaminski[1], F. Rohrer[1], R. Tillmann[1], A. Wahner[1], R. Wegener[1], Z. Yu[1], and A. Kiendler-Scharr[1]

[1]Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany
[a]now at: Max Planck Institute for Chemistry, Department for Multiphase Chemistry, Mainz, Germany
[*]These authors contributed equally to this work.

Received: 13 October 2015 – Accepted: 24 October 2015 – Published: 16 November 2015

Correspondence to: A. Kiendler-Scharr (a.kiendler-scharr@fz-juelich.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

A new PLant chamber Unit for Simulation (PLUS) for use with the atmosphere simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction Chamber) has been build and characterized at the Forschungszentrum Jülich GmbH, Germany. The PLUS chamber is an environmentally controlled flow through plant chamber. Inside PLUS the natural blend of biogenic emissions of trees are mixed with synthetic air and are transferred to the SAPHIR chamber where the atmospheric chemistry and the impact of biogenic volatile organic compounds (BVOC) can be studied in detail. In PLUS all important enviromental parameters (e.g. temperature, PAR, soil RH etc.) are well-controlled. The gas exchange volume of 9.32 m^3 which encloses the stem and the leafes of the plants is constructed such that gases are exposed to FEP Teflon film and other Teflon surfaces only to minimize any potential losses of BVOCs in the chamber. Solar radiation is simulated using 15 LED panels which have an emission strength up to 800 $\mu mol\,m^{-2}\,s^{-1}$. Results of the initial characterization experiments are presented in detail. Background concentrations, mixing inside the gas exchange volume, and transfer rate of volatile organic compounds (VOC) through PLUS under different humidity conditions are explored. Typical plant characteristics such as light and temperature dependent BVOC emissions are studied using six *Quercus Ilex* trees and compared to previous studies. Results of an initial ozonolysis experiment of BVOC emissions from *Quercus Ilex* at typical atmospheric concentrations inside SAPHIR are presented to demonstrate a typical experimental set up and the utility of the newly added plant chamber.

1 Introduction

Volatile organic compounds (VOC) impact on atmospheric chemistry and are involved in O_3, oxygenated VOC (OVOC), and secondary organic aerosol (SOA) formation (Seinfeld and Pandis, 1998). Biogenic VOC (BVOC) account for the majority (~ 90 %) of annually emitted VOC globally (Guenther, 2002) with isoprene identified as the single most important BVOC (Steiner and Goldstein, 2007). Despite numerous activities exploring the impact of BVOC on atmospheric chemistry, many uncertainties remain. For instance isoprene has only recently been found a key species in OH recycling in low NO_x environments (Hofzumahaus et al., 2009; Lelieveld et al., 2008) with exact processes leading to this recycling still being uncertain. Isoprene was found to suppress new particle formation from BVOC photo-oxidation (Kiendler-Scharr et al., 2012, 2009), while constitutive and stress-induced mono- and sesquiterpene emissions contribute to photo-chemical particle number and mass formation (Hallquist et al., 2009; Mentel et al., 2013, 2009). Also field studies have repeatedly shown that the total reactivity of air masses towards OH is larger than can be explained based on measurements of individual compounds reactive to OH e.g. (Di Carlo et al., 2004; Edwards et al., 2013; Noelscher et al., 2012; Whalley et al., 2011). This gap in OH reactivity may be either explained due to direct emissions or atmospheric oxidation products that are currently not identified as single compounds. It is plausible that large sources of organic compounds have not yet been identified (Goldstein and Galbally, 2007; Hallquist et al., 2009). This lack in understanding of BVOC sources may limit bottom-up estimates of SOA formation and OVOC such as e.g. acetone.

Due to the importance of BVOC for atmospheric chemistry and the large remaining gaps in process level understanding, BVOC are a subject of continuous research. One concern with investigations of BVOC and their impact on atmospheric chemistry arises from the fact that under natural conditions BVOCs are emitted as complex blends, whereas many simulation chamber experiments use single BVOC or simple mixtures to explore atmospheric chemistry processes. The use of direct emissions of plants is a way of progressing towards more realistic experimental simulations. Recently a number of set ups implementing the use of direct plant emissions in atmospheric chemistry experiments have emerged, ranging from the investigation of BVOC oxidation within a greenhouse (Joutsensaari et al., 2005; Pinto et al., 2007) to designs implementing two separate chambers for independent variation of emission and oxidation conditions (Hao et al., 2009; Mentel et al., 2009; Timkovsky et al., 2014; VanReken et al., 2006).

Here we present details of the design and implementation of a PLant chamber Unit for Simulation (PLUS) for use with our atmosphere simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction Chamber). The PLUS chamber set-up is described in detail and characterization experiments quantifying VOC transfer efficiencies and plant emission behavior as function of key physiological parameters are discussed. An example of an ozonolysis experiment in SAPHIR using PLUS as BVOC source is given to show how such experiments can be used to quantify BVOC impacts on atmospheric composition.

2 Facility description

Experiments were conducted in the atmosphere simulation chamber SAPHIR coupled with a newly developed plant chamber PLUS in Jülich, Germany. In brief SAPHIR consist of a double walled Teflon (FEP) film of cylindrical shape (volume 270 m^3) and is used for simulation experiments studying atmospheric chemistry processes under atmospherically relevant conditions. Representative concentration ranges for experiments are ensured by using ultra-pure zero air, generated from evaporated liquid nitrogen and oxygen (Linde, purity 99.99990 %). To this clean, dry air, trace gases are added according to experiment purpose. The SAPHIR chamber is described in more details elsewhere (Bohn et al., 2005; Rohrer et al., 2005; Schlosser et al., 2009).

The PLUS facility consists of three containers which are installed beneath the SAPHIR chamber. The first container is the gas exchange chamber which houses the plants. When used for experiments with SAPHIR this chamber is operated with air from the Linde ultra-high pure zero air supply. A second container houses the process control system including standard instrumentation monitoring plant chamber environmental conditions. The third container houses a system to purify ambient air from NO_x, O_3, VOC, and particles. This air can be used to supply the gas exchange chamber with cleaned outside air instead of zero air. All three components of PLUS are described in more detail in the following sections.

2.1 PLUS plant container design and implementation

A schematic of the container housing the PLUS plant container is shown in Fig. 1. The custom built container (Ilkazell Isoliertechnik GmbH, Zwickau, Germany) is gas tight and temperature and light controlled with outer dimensions of 2.39 m × 3.84 m × 2.84 m. Special emphasis of the dynamic plant chamber setup was on contamination-free operation, with some of the contamination prevention strategies being adopted from SAPHIR. The walls of the container have a layered structure to provide good thermal insulation while limiting the risk of outgassing from wall materials (see Fig. 2). From the outside to the inside the wall is built of: (i) an outer steel housing, (ii) a spray foam insulation of 120 mm thickness, (iii) a stainless steel wall, (iv) an air buffer volume, and (v) a gas tight welded stainless steel containment. The side- and back-walls as well as the floor of this inner containment are made of double-walled (pre-inflated) stainless steel heat exchange panels. Temperature control inside the container is achieved by adjusting the temperature (0 to 50 °C) of the water-based thermofluid with an externally installed heating/cooling unit (Unistat Chiller, Typ 055T-H-TP35, Huber, Germany).

The inner volume of the container is divided in three hermetically separated compartments: (i) a light control unit, (ii) the gas exchange unit, and (iii) an interspace also housing the soil. These three compartments are described in more detailed in the following.

The light control unit is hermetically separated from the gas exchange unit by means of five glass window panes. Window pane gaskets are made of Viton. The light needed for photosynthesis activity is provided by 15 LED panels (Typ SL3500, Photon Systems Instruments, Czech Republic). Five rows with three LED panels in each row are installed on a movable frame ensuring homogenous illumination of the chamber. The intensity of each LED panel can be controlled individually by the process control unit. Intensity of Photosynthetic Active Radiation (PAR) is 0 to 800 μmol m^{-2} s^{-1}, as measured at a distance of 1 m. The compartment for the light control unit is air conditioned by means of an external air cooling system (5.5 kW, Robert Schiessel GmbH, Germany). Recirculating air through the external cooler sustains an (adjustable) continuous underpressure of ~ 200 Pa with respect to the gas exchange unit, to assure mass transfer out of the gas exchange unit in case of any leakage on the window panes. An ultrasonic sound leak test proved the tightness of the glass windows.

The gas exchange unit is set up as follows. A rectangular aluminum frame inside the chamber provides the frame for the 1.80 m × 3.52 m × 1.45 m gas exchange volume. Teflon film (FEP, 75 µm thickness, Vector Foiltec, Bremen, Germany) is mounted across each side and the ceiling of the frame separately. The side wall and the ceiling of the frame were assembled such that the inside of the frame is exposed to the FEP film only. The bottom part of the frame is constructed as a table like structure where the surface of the table, except for the holes where the plant stem and leaves reach into the gas exchange volume, is also completely covered with the FEP film. The seal of this table against the frame is achieved by a silicone-based pneumatic gasket (Flohreus GmbH) which is installed along a groove in the rim of the table. While inflated (up to 2 bar) the pneumatic gasket presses the FEP film of the table against the FEP film of the frame. When plants are installed in the gas exchange chamber the stem and leaves are protruding through one of six holes in the table into the gas exchange volume while the soil is kept beneath the table. Each hole is sealed by fusing a rectangular piece of the FEP film around the stem of a plant separating the soil of the upper parts of the plant. The piece of rectangular FEP film is then pressed onto the FEP film covering the table using a Teflon ring with a Viton O-ring.

The space around the sealed gas exchange unit is called the interspace. The interspace houses all necessary connections for the installed sensors (e.g. light and temperature sensors), the plant pots including soil, tubing for the air supply, and the irrigation system. To ensure a low gaseous contaminant level, all cables and the tubing are either made of Teflon or have a Teflon cover. The plant pots are made of stainless steel. The interspace is furthermore continuously flushed with high purity air (up to 1 m^3 h^{-1}) and kept at 31 Pa below the gas exchange unit to avoid transfer of gases from this compartment to the gas exchange unit.

The new plant chamber PLUS is run in dynamic mode, which means that it is continuously flushed with purge air to (i) sustain CO_2 for photosynthetic activity of enclosed plants and (ii) allow purging of emitted trace gases and water vapour. The air supply (see Sect. 2.3 for details) is distributed inside the gas exchange unit using six Teflon tubes with an ID of 0.5 inch. Each tube is connected to a Teflon nozzle (0.25 inch ID). Three nozzles are distributed along each side of the plant table which introduces synthetic air into the gas exchange volume. Through the nozzles flow of air into the gas exchange unit is turbulent, thus ensuring homogeneous mixing.

Air from PLUS can be transferred to SAPHIR via a transfer line tube with an inner diameter of 80 mm and a length of 1.89 m that connects the back plane of the gas exchange unit with the bottom plane of SAPHIR (see Fig. 1). The tube is made of Perfluoralkoxy-Polymere (PFA) and temperature controlled (typically 60 °C). Directly prior to the inlet to SAPHIR, two wide-bore valves are situated: one controls the flow towards SAPHIR, the other towards ambient. While only PLUS related experiments are conducted the air flow is usually directed to the ambient. To prevent pressure fluctuations within the plant chamber by valve switching, the opening width (resistance) of the exhaust valve can be adjusted by a pneumatic positioner, so to mimic the internal counter-pressure of SAPHIR. The adjustable positioners implemented in both of the transfer tube valves also allows dynamic operation of SAPHIR, i.e. only a fraction of VOC-loaded PLUS air may be introduced into SAPHIR, while the residual can be vented to ambient. When plants are installed in PLUS, continuous flow through the gas exchange unit ensures that the plants are supplied with CO_2 and that the emissions of the plants are continuously flushed out of the gas exchange unit.

The flow through the gas exchange unit is adjustable between 0 and 42 m^3 h^{-1}. Normal operations flows are usually between 6 and 30 m^3 h^{-1}. The pressure inside the gas exchange unit is usually kept at 56 ± 5 Pa over atmospheric pressure. The interspace is also flushed continuously 1 m^3 h^{-1} from the same air supply. Here, a process-controlled small-bore proportional valve (Typ 6024, nominal bore 12 mm, Bürkert GmbH & CO KG, Germany) is installed to adjust the pressure-difference between the interspace surrounding the gas exchange unit and ambient atmosphere. The pressure in the interspace is kept at a constant pressure of 25 ± 2 Pa over atmosphere. Differential pressures are monitored by means of two fully metal-sealed differential pressure gauges (Type Barathon 226A, 200 Pa, MKS, Germany), to control the PLUS pressure gradients. All three valves (plant chamber exhausts and sheath air exhaust) are process-controlled, i.e., the desired pressure differences can be set and are controlled by a feedback control loop in the automatic process control system. The stepwise increase in overpressure from ambient conditions outside the chamber to 56 Pa in the gas exchange unit prevents diffusion of possible contaminants from the outside into the gas exchange unit. The pressure of the PLUS gas exchange unit is always kept 6 ± 2 Pa above the pressure in the SAPHIR chamber. This pressure difference ensures flow from the PLUS gas exchange volume to SAPHIR while PLUS is coupled to SAPHIR.

2.2 Air supply and mixing

Two air supply systems can be used for the gas exchange chamber, the SAPHIR air supply and a system utilizing cleaned outside air. As mentioned above the air supply used for SAPHIR bases on mixing O_2 and N_2 from liquid reservoirs (Linde, purity 99.99990 %). This ultra-clean air can be used for PLUS when CO_2 is added at the gas exchange chamber inlet to supply the plants with.

Usually for standby operation of the PLUS plant chamber cleaned outside air is used. Ambient air is compressed into a stainless steel buffer volume (500 liters, 7 bar) by means of four oil-free scroll pumps (Mark, OFMS 15). The large bore (100 mm ID) inlet tube of the compressor is made from stainless steel and has a recyclable stainless steel mesh filter cartridge (1 µm pore size) for aerosols, which is built into a stainless steel housing installed outdoors at ca. 2 m above ground. The compressed air is dried to a dew point of typically below −40 °C using two columns of molecular sieve and is subsequently scrubbed from VOC contaminants by means of an additional column filled with activated charcoal (both Zander KA-MT 10-95). Highly volatile organic compounds, which might break through this first purification stage are removed by a second stage heated VOC converter (Bekokat Typ CC-120, Beko, Germany). Aerosols are removed by two pure Teflon particle filter units (FEP/PTFE, Fluoroflow 33-14710-002-5-E, with 0.2 µm cut off size and 33-14710-825-5-E with 0.05 µm cut off size, Parker Hannifin GmbH, USA) installed in stainless steel housings (VBA-111-BE, Parker Hannifin GmbH, USA).

Trace gases like, e.g., CO_2, VOC, and water vapour can individually be added to the air supply. Both, VOC standard compounds and CO_2 are added from gas bottles to the synthetic air flow. Mixing ratios of both additions are controlled by two Mass Flow Controllers (Mass Stream D-6311, Bronkhorst, Germany). CO_2 concentration at the PLUS inlet is kept at the upper range of natural occurring conditions of about 500 ppm to maintain vital photosynthesis. Dependent on the mass flow rate through the chamber and the amount of leaf biomass installed, typical CO_2 mixing ratios at the outlet (and representative of inside chamber) are about 450 ppm. Water vapor can be added to the purge air by vapourization of purified (Milli-Q, Millipore Corporation) water in a 25 mm outer diameter stainless steel tube with a length of 30 cm which is heated to 350 °C. Adjusting the liquid flow sustained by a peristaltic pump relative humidity of the purge air can be varied between 0 and 100 %.

2.3 Process control unit and analytical instrumentation

For ease of user operation the PLUS facility is equipped with an automated control process unit and standard instrumentation used to monitor environmental conditions and trace gas exchange. All process control is based on industrial software and hardware (S7, Siemens, Germany). Parameter settings (flow rate and direction, gas addition, light intensity, temperature, pressure gradients, soil water content etc.) can be set by an automatic process control system, or follow pre-programmed adjustable diel courses. For most of these parameters two-stage (alarm and shut down, respectively) upper and lower threshold levels are preset for cases of mal-operation and/or mal-function.

Pressures inside the PLUS chamber are monitored by pressure gauges (MKS Barathon 226A). As mentioned before, transfer of air from the PLUS gas exchange chamber to SAPHIR is ensured by relative over pressures. These are monitored continuously and upper and lower threshold values are defined as shut down criteria. Light intensity in the chamber is varied by regulating the output of the LED panels between 0 and 100 %. Monitoring of the light intensity is provided using a quantum sensor (LI-190SZ-50, LI-COR GmbH, Germany) installed inside the gas exchange volume situated in the center of the plant table at about canopy height of the installed plants. Distributed over the “canopy height” of installed plants, a set of 6 leaf temperature sensors (Type K) is applied to measure leaf temperature. Gas temperature inside the gas exchange volume is measured also by a Type K temperature sensor which is located approximately in the center (height, lengh and width wise) of the gas exchange volume. The soil moisture of each plant is measured individually using a moisture sensor (UMS GmbH München, EC-5). The irrigation system is automated such that water is dripping into the plant pot if the soil moisture falls below a threshold value until the soil moisture rises above a defined threshold.

For gas phase measurements a sampling line (6 mm Teflon tube) is installed 15 cm next to the transfer line tube. The position of the outlet line is chosen such that the measurements at the outlet are representative of the gas mixture transferred through the transfer line tube. A second sampling line (6 mm Teflon tube) is connected to the PLUS inlet where the air mixture can be measured before it enters the gas exchange unit.

Gas phase CO_2 and water vapor concentration are measured at the PLUS inlet and outlet by Cavity Ring Down Spectroscopy (CRDS, Picarro, Model G2301). Measurements for the inlet and outlet are obtained by switching via a valve system between both measurement ports. This allows for continuous measurement of the plants transpiration and respiration rates. VOC mixing ratios are measured using a Proton-Transfer-Reaction Time-of-Flight Mass-Spectrometer (PTR-ToF-MS, Ionicon, Austria, Jordan et al., 2009). A valve system is used to switch the measurement point of the

PTR-ToF-MS between PLUS inlet, PLUS outlet, and the SAPHIR chamber. Calibrations were performed with diffusion sources. The sensitivity of the instrument as checked by custom-made compressed gas standard containing about 670 ppb of isoprene, α-pinene, acetone, other carbonyl compounds and aromatics. The gas standard was diluted to mixing ratios from 2–13 ppb by means of an advanced liquid calibration unit (LCUa, Ionicon, Austria). For the accuracy of the VOC measurement see Table 2. For VOC specification two GC/MS/FID systems (7890N GC, 5975 B/C MS, Agilent, USA) are directly coupled to SAPHIR (Kaminski, 2014). Samples were taken every 30 min by an online thermal desorption unit (TDSG, Gerstel, Germany). The GC systems were specifically optimized for the quantification of labile BVOCs using silanized surfaces. Ozone was removed in the enrichment system by chemical titration with NO. The substance identification was done by the comparison of the samples with certified standard gas mixtures (Apel-Riemer Environmental Inc, USA). In cases where no authentic standards were available the substances were identified by using the specific mass spectra or in case of the monoterpenes by using kovats indices. Due to its excellent signal stability the FID signal was used for compound quantification.

3 Characterization experiments and results

3.1 Temperature and flow stability

As mentioned the temperature inside the PLUS chamber is adjusted and controlled using heat exchangers at the floor and three walls of the container. While this system has relatively slow response to changes in temperature set points (1–3 °C $\mathrm{h^{-1}}$, see Table 1), it provides good temperature stability in the range 13–35 °C. The system thus allows for the investigation of temperature dependence of biogenic emissions (see below). Table 1 provides further details on the temperature and flow stability performance of PLUS.

3.2 Gas purity and background concentrations

After two days of flushing the empty gas exchange chamber with synthetic air from the Linde supply, the purity of gas exiting the gas exchange volume was determined by measuring with the PTR-ToF-MS at the inlet and outlet of the gas exchange chamber (see Fig. 1). The PTR-ToF-MS was switched between measuring 15 min at the PLUS inlet and 105 min at the PLUS outlet for a total duration of 12 h. The difference in concentration between the outlet and inlet measurements determines the type and level of contamination inside of the plant gas exchange volume. A relative increase of 48 pptv of Acetone between the PLUS inlet and outlet was detected being the compound with the largest contribution. Also Isoprene was identified with a relative contribution of 14 pptv. No other significant contamination could be detected. The most likely source for these compounds inside the plant gas exchange volume is the silicon based pneumatic seal which seals the plant table against the frame of the gas exchange volume. Overall contaminant concentrations in the lower ppt range are about 3 orders of magnitude lower than VOC emitted biogenically, and can be considered negligible for the purpose of our atmosphere simulation experiments.

3.3 Mixing in the PLUS gas exchange volume

To ensure quantitative transfer of plant emitted BVOC to the SAPHIR simulation chamber turbulent conditions in the gas exchange unit are sought. Mixing behavior in the gas exchange chamber was studied by the flush out behavior of CO_2, acetone, α-pinene, and nopinone. CO_2 was used as a conservative, chemically inert tracer not interacting with wall surfaces. For this experiment the chamber was purged with a relatively low air flow rate ($100\,\mathrm{L\,min^{-1}}$) to exert a relatively low air speed in the inlet nozzles and long residence time within the chamber of about 90 min, respectively. CO_2 and VOC were added to the flow of synthetic air until constant concentrations were reached inside the gas exchange volume. Concentrations for CO_2, acetone, α-pinene and nopinone were 455 ppm, 83, 78, and 86 ppb, respectively. Then addition of CO_2 and VOC to the synthetic air was stopped while the flow of synthetic air was kept constant at 100 L min^{-1}. Assuming perfect mixing the trace gas concentration should depend on the flow of synthetic air in the chamber and the volume of the chamber only and is expected to follow an exponential decrease.

$$C_t = C_{t-1} \times e^{\left(-\frac{Q_{\mathrm{PLUS},t}}{V_{\mathrm{PLUS}}}\right)}, \tag{1}$$

with C_t being the trace gas concentration at the time t, C_{t-1} the concentration at the previous time step, $Q_{\mathrm{PLUS},t}$ the flow through the gas exchange volume at time t, V_{PLUS} the volume of the gas exchange volume. Figure 3 shows the change in concentration, ln(C_t) vs. time for CO$_2$, acetone, α-pinene and nopinone in the gas exchange volume as measured and calculated. Inhomogeneous mixing in the gas exchange volume (e.g., by stratification or air pockets/regions inside the chamber where CO$_2$-rich or VOC-rich air remains) would result in deviation from the expected exponential concentration decrease. The ln(C_t) decreased linear over a period of approximately 8 h, equivalent to exchanging the gas volume in the chamber 5 times. No significant deviations from the exponential decrease in the trace gas concentration could be observed during this time period. Therefore we can assume that the gas exchange chamber is well mixed by using turbulent mixing from the six injection nozzles in the plant table. Note that no significant difference between CO$_2$ and VOC was observed, indicating that in the time range explored VOC are not lost on chamber walls.

Additionally the CO$_2$ flush out was also used to determine the effective volume of the gas exchange chamber. Applying a linear fit to the CO$_2$ concentration and using an average of the flow into the chamber during the first 5 h of the experiment the effective volume of the chamber was determined to 9.32 ± 0.5 m^3, in agreement with the geometric volume of the gas exchange unit of 9.187 m^3.

3.4 Transfer efficiency of selected VOC at different relative humidity

The transfer efficiency of the complete system of SAPHIR-PLUS was studied using a self-prepared gas standard. The gas standard consisted of acetone, isoprene, α-pinene, nopinone, and methyl salicylate (MeSa) in N_2 (99.999 % purity). The compounds were chosen to represent on the one hand typical BVOC emissions (isoprene, α-pinene, MeSa) and on the other hand a significant variety in molecular masses, boiling point and solubility in water (see Table 3).

At the start of the experiment CO_2, VOC from the gas standard, and water vapor were added to the synthetic air flowing into the chamber. No plants were installed during this experiment. The air flow into the chamber was $100\,\mathrm{L\,min^{-1}}$. The additional flow of VOCs into the synthetic air was chosen such that a constant concentration of about 70 ppbV for each compound was reached inside the PLUS gas exchange volume. A CO_2 concentration of ~ 455 ppmV was maintained in the PLUS exchange volume throughout the experiment.

The addition of water to the synthetic air was varied during the experiment to achieve different relative humidity levels while the VOC concentration was kept constant. In total four different relative humidity levels (25 to 100 %) were chosen for this experiment. Once a stable RH was achieved inside the gas exchange unit, PLUS was coupled to SAPHIR and VOC, CO_2 and water vapor were transferred from PLUS to SAPHIR. For practical reasons the sequence of experiments was started with RH of 64 %, stepwise decreasing to 50 and 25 % by dilution. In a second experiment the transfer efficiency was examined starting at 100 % RH. Note that the RH in SAPHIR was little affected by the injection of air from PLUS. The RH changed in SAPHIR from 1 to about 7 % RH for the first experiment and 0.5 to 3 % for the second experiment.

For evaluation of the transfer efficiency, VOC concentrations were measured by PTR-ToF-MS with a one minute time resolution switching between the PLUS inlet and PLUS outlet and then subsequently between PLUS outlet and SAPHIR. After starting VOC addition the concentration at the PLUS inlet was monitored for about 1 h to verify a stable concentration of VOC in the inlet flow. Then the PTR-ToF-MS measurements were switched repeatedly to measure between the PLUS outlet and SAPHIR. The VOC concentrations at the PLUS outlet were measured for 20 min before switching for 40 min to the SAPHIR outlet thus one measurement cycle was 1 h. The coupling of PLUS to SAPHIR was maintained for approximately one hour, ensuring that concentration changes in SAPHIR due to continuous inflow of VOC rich air could be measured.

After one hour PLUS was decoupled from SAPHIR and the RH was changed. This procedure was repeated for all different RH values. Throughout the experiment the CO_2 was used as an inert tracer and measured switching continuously between the PLUS inlet and outlet with one Picarro instrument and separately with a second Pircarro system in SAPHIR. The transfer efficiencies between PLUS inlet and outlet and between PLUS outlet and SAPHIR were determined by the ratio of the measured VOC and CO_2 concentration divided by the calculated concentration. The calculated concentration for PLUS was derived, taking the initial concentrations measured at the PLUS inlet and calculating the concentration inside the gas exchange volume depending only on the flow and the volume.

$$C_{\mathrm{PLUS},t} = C_{\mathrm{inlet},t} \times \frac{Q_{\mathrm{PLUS},t}}{V_{\mathrm{PLUS}}} + C_{\mathrm{PLUS},t-1} \times e^{\left(-\frac{Q_{\mathrm{PLUS},t}}{V_{\mathrm{PLUS}}}\right)}, \tag{2}$$

with $C_{\mathrm{PLUS},t}$ being the calculated concentration in the gas exchange volume at time t, $C_{\mathrm{inlet},t}$ the VOC concentration at the PLUS inlet at time t, $Q_{\mathrm{PLUS},t}$ the flow through the gas exchange volume, V_{PLUS} the volume of the gas exchange volume, and $C_{\mathrm{PLUS},t-1}$ the previously calculated VOC concentration in the gas exchange volume. Similarly, the calculated concentration in SAPHIR was determined, taking the initial concentration in PLUS and calculating depending on flow from PLUS into SAPHIR and on the volume of SAPHIR.

$$C_{\mathrm{SAPHIR},t} = C_{\mathrm{PLUS},t} \times \frac{Q_{\mathrm{PLUS},t}}{V_{\mathrm{SAPHIR}}} + C_{\mathrm{SAPHIR},t-1} \times e^{\left(-\frac{Q_{\mathrm{SAPHIR},t}}{V_{\mathrm{SAPHIR}}}\right)}, \tag{3}$$

with $C_{\mathrm{SAPHIR},t}$ being the calucalted VOC concentration in SAPHIR at time t, $C_{\mathrm{PLUS},t}$ the measured VOC concentration in the gas exchange volume, $Q_{\mathrm{PLUS},t}$ the flow from the gas exchange volume into SAPHIR, V_{SAPHIR} the volume of SAPHIR, $C_{\mathrm{SAPHIR},t-1}$ the calculated VOC concentration in SAPHIR at the previous time step, $Q_{\mathrm{SAPHIR},t}$ the dilution flow of SAPHIR that compensates for sampling and leakage. Figure 4 shows the result for both transfer efficiency measurements (upper panel between PLUS inlet and outlet, lower panel between PLUS and SAPHIR) in dependence of the RH levels. The inert tracer CO_2 had a transfer efficiency of about 1 for both systems. Since the only losses processes for CO2 are due to leakage between the PLUS gas exchange volume and the intermediate flushed space or between PLUS and SAPHIR it can be concluded that losses due to leakages are negligible in this system. The transfer efficiencies for VOC between PLUS inlet and PLUS outlet were on average 0.85 with the lowest value being 0.81. For regular operation as plant chamber this transfer is of minor importance, as the PLUS inlet is operated with VOC free air under these conditions. The transfer efficiencies from PLUS inlet to PLUS outlet and from PLUS outlet to SAPHIR are comparable. However slightly lower at an average of 0.8 with the lowest value of 0.59 observed at 65 % RH. Note that this lowest value was observed for the first stage of the experiment, when transfer lines between PLUS and SAPHIR were not conditioned for VOC.

It is important to note that there is no significant difference in the transfer efficiencies for different VOC, indicating that within the range of vapor pressure and polarity investigated here, VOC mixtures emitted from trees enclosed in the gas exchange unit, are transferred to SAPHIR without changes to the relative composition of the VOC mixture. Transfer is furthermore independent of relative humidity in the range of 25 to 100 % for both transfer between PLUS inlet and outlet and transfer between PLUS and SAPHIR.

Coupling of PLUS to SAPHIR for transfer of BVOC emitted from trees is achieved by either continuously transferring air from PLUS to SAPHIR or by a short pulsed coupling (time scale several minutes to hours). Figure 5 displays the temporal evolution of monoterpenes emitted from six *Quercus Ilex* trees. The upper panel shows monoterpene mixing ratios in PLUS together with light intensity (yellow area). The lower panel shows resulting monoterpene concentrations in SAPHIR when a continuous flow of 30 $m^3 h^{-1}$ was fed from PLUS to SAPHIR. Also shown is the calculated monoterpene concentration applying Eq. (3) to derive monoterpene concentration in SAPHIR. Note that here a transfer efficiency of 1 is implicitly assumed. Apart from the very beginning of the experiment, where calculated monoterpene concentration exceeds observed ones, good agreement is found. At these early times, chamber mixing times may play a role. The overall mixing time of SAPHIR for uniform mixing is 5 min, limiting the ability to observe fast changes in concentration of the inflow from PLUS.

3.5 Light and temperature dependent plant emissions

To evaluate BVOC emission characteristics inside PLUS, six potted Mediterranean holm oak (*Quercus Ilex*) trees were installed in the plant chamber. *Quercus Ilex* is a strong monoterpene emitter with emissions being light dependent (Kesselmeier and Staudt, 1999 and references therein). The main compounds emitted from the plants during our experiments were α-pinene, β-pinene, Z-β-Ocimene, and limonene as determined by GC-MS/FID (see Fig. 6) in agreement with observations from laboratory plant enclosure and field studies (e.g., Blanch et al., 2007; Llusià and Peñuelas, 1999).

To determine the dependence of emissions on light and temperature, diel courses of light and temperature were pre-set with 12 h day/night periods (Fig. 7). To simulate field conditions the light intensity was gradually increased over a period of 6 h, followed by a 6 h gradual decrease. VOC emissions were analyzed as function of temperature (13–31 °C) for periods of up to 3 consecutive days at one temperature.

Figure 7 shows the dependence of the normalized ($C/C_{l,\max}$) emissions on light intensity at different temperatures, confirming the well-known strong light-response of isoprenoid emissions by *Quercus ilex*. Total emissions are zero while lights are off in PLUS and increase with increasing light intensity. The maximum concentration of isoprene and monoterpenes in PLUS was reached shortly after the light maximum. Normalized isoprene and monoterpene emissions revealed similar responses to the diel course of light intensity in all temperature regimes. Methanol, however, showed emission pulses after the onset of illumination, as has been observed previously for different plant species both in field and laboratory experiments under controlled conditions (Folkers et al., 2008; Nemecek-Marshall et al., 1995; Warneke et al., 2002). Morning pulses of methanol emissions were explained as a consequence of accumulation in extracellular water of the plant's apoplast when stomata are closed during nighttime (Niinemets and Reichstein, 2003). Methanol is continuously produced and high aqueous phase concentrations built up in the aqueous phase during nighttime when stomata are closed. In the morning, stomata open and methanol is released until equilibrium is reached between the gas phase of the substomatal cavity and the atmosphere. ^{13}C-labelling experiments confirmed that the PAR dependence of methanol emissions is not directly linked ($< 10\,\%$) to photosynthetic de novo production, but rather originates from precursor compounds with long-turnover times for carbon, such as cell wall components (Folkers et al., 2008). Methanol emissions are generally associated with plant growth (Fall and Benson, 1996; Hueve et al., 2007; Nemecek-Marshall et al., 1995; Obendorf et al., 1990). Methanol emission have been shown to be temperature dependent in general (Folkers et al., 2008). Note that due to the increase of methanol emissions with increasing temperature (see also below), the relative importance of the morning emissions gradually vanished in PLUS with increasing temperature (Fig. 7).

The same set of experiments was used to study the temperature dependence of the *Quercus Ilex* emissions. Figure 8 shows the concentrations of isoprene, the sum of the monoterpenes and methanol normalized to the concentrations at 30 °C vs. temperature in PLUS. The four hour averaged data of peak emissions of isoprene and the monoterpene followed a well-described exponential increase with increasing temperature (e.g. Guenther et al., 1993). For monoterpenes the emissions increased with a slope (β in Eq. 5 in Guenther et al., 1993) of 0.11 ± 0.02 which is in good agreement with literature (Staudt and Bertin, 1998). Methanol increased linearly with temperature with a 10 % increase of peak emissions every ∼ 4 °C between 13 and 31 °C. Note that for these experiments the plants were kept in the plant chamber undisturbed for 109 consecutive days. During that time period the plants show no signs of stress effects.

3.6 BVOC ozonolysis of real plant emissions

To illustrate the applicability of SAPHIR-PLUS as a facility for simulation of atmospheric chemistry processes and impacts of BVOC emissions the following experiment was conducted. After pulsed injection of *Quercus Ilex* emissions from PLUS to SAPHIR for 3.5 h, PLUS was decoupled from SAPHIR and an ozonolysis experiment in SAPHIR was performed (Fig. 9). Ozonolysis of BVOC is known to be a source of OVOC and SOA in the atmosphere. One OVOC of interest in this respect is acetone, as it is relatively long lived (global mean lifetime several weeks), and serves as source of HO_x and PAN in the upper troposphere (Gierczak et al., 1998; Jacob et al., 2002). As can be seen in Fig. 9 (lower panel) the ozonolysis of the monoterpene mixture leads to production of acetone with a maximum concentration gain of 0.68 ppb. Considering dilution in SAPHIR this observed acetone production is equivalent to an overall yield of 18.8 % from the mixed monoterpene emissions form *Quercus Ilex*. This yield can be evaluated taking known acetone yields of individual monoterpenes and their relative contributions to *Quercus Ilex* emissions (Fig. 6) into account. As no OH scavenger was used in these experiments, the monoterpene are oxidized by OH and ozone. From the decay curve of the individual monoterpenes, it can be estimated that 17 up to 64 % of the monoterpenes were oxidized by OH, depending on the substance. Based on upper limits in the literature (Atkinson and Arey, 2003) a weighted average molar yield of 17 % is expected from the mixture used in this experiment (see Table 4). This takes relative contributions from ozone and OH oxidation into account. Considering that some acetone could have been produced from compounds which were not measured, such as plant emitted sesquiterpenes or intermediate oxidation products, the observed 18.8 % acetone yield is in good agreement with upper estimates from literature data. With overall concentrations in the range of atmospheric conditions, this combined contribution of ozone and OH to monoterpene oxidation and product formation may still be considered representative for BVOC oxidation in low NO_x environments. This experiment thus exemplarily shows that using direct emissions of plants as BVOC source, a simulation of atmospheric chemistry can be used to derive representative product yields for use in bottom up estimates of global sources.

4 Conclusion

A new plant chamber for use as source of direct emissions from plants in atmospheric chemistry simulation experiments was set up at SAPHIR. Technical features and implementation of PLUS are described in detail. PLUS is shown to provide an environment in which parameters of importance for plant physiology can be chosen at environmental importance. The emissions from *Quercus Ilex* as function of both light and temperature observed in the gas exchange chamber are representative of emissions observed in ambient studies. Therefore PLUS can be considered a representative source of BVOC emission mixtures. VOC mixtures were shown to be quantitatively transferred to SAPHIR, ensuring the emission pattern remains unchanged. In an ozonolysis experiment the total yield of acetone from oxidation of *Quercus Ilex* emissions was determined. Future applications of SAPHIR-PLUS can therefore target a wide spectrum of atmospheric chemistry questions ranging from product yield determination (OVOC and SOA), oxidation cycles and oxidant (OH) recycling, to the evaluation of total OH reactivity of both direct emissions and their oxidation products under a variety of oxidation regimes.

Acknowledgements. We gratefully acknowledge Theo Brauers (IEK-8, Forschungszentrum Jülich), Knut Dahlhoff (ZEA-1, Forschungszentrum Jülich), and Jürgen Wildt (IBG-2, Forschungszentrum Jülich) for their valuable contributions to discussions on the design of PLUS. Alfred Budwig (ZEA1, Forschungszentrum Jülich) implemented the user control system (S7).

The article processing charges for this open-access publication were covered by a Research Centre of the Helmholtz Association.

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Table 1. Temperature and Flow Stability for typical operational conditions with $T_{\mathrm{PLUS}} = 20\,^{\circ}\mathrm{C}$ and $Q_{\mathrm{PLUS}} = 500\,\mathrm{L\,min^{-1}}$.

Environmental Conditions	Value
Temperature Stability without influence of LED-Lamps	$T_{\mathrm{PLUS}} \pm 0.75\,^{\circ}\mathrm{C}$
Temperature Stability with influence of LED-Lamps	$T_{\mathrm{PLUS,LED}} \pm 1.5\,^{\circ}\mathrm{C}$
PLUS Temperature Heating/Cooling Rate	$1.3\,^{\circ}\mathrm{C\,h^{-1}}$
Flow PLUS Inlet	$Q_{\mathrm{PLUS}} \pm 5\,\mathrm{L\,min^{-1}}$
Flow PLUS Outlet	$Q_{\mathrm{PLUS}} \pm 22\,\mathrm{L\,min^{-1}}$

Table 2. LOD and Accuracy (3δ error of the sensitivity) of calibration-based PTR-TOF-MS measurements for VOCs of interest.

VOC	Methanol	Acetaldehyde	Acetone	Isoprene	α-pinene	Nopinone
LOD [ppt]	601.42	218.37	97.78	80.70	60.12	24.61
Accuracy [%]	8.06	6.48	4.08	4.25	3.89	5.06

Table 3. Summary of physical and chemical properties of VOC (acetone, isoprene, α-pinene, nopinone, and methyl salicylate) used in gas standard for transfer efficiency characterization.

VOC	Molecular formula	Molar mass mass	Boiling point (K)	k°_H at 298.15 K ($mol\,kg^{-1}\,bar^{-1}$)
Acetone	C_3H_6O	58	329.3 ± 0.3[a]	25[a]
Isoprene	C_5H_8	68	307 ± 2[a]	0.036 ± 0.003[b]
α-pinene	$C_{10}H_{16}$	136	430 ± 4[a]	0.029 ± 0.004[b]
Nopinone	$C_9H_{14}O$	138	482.15[c]	195 ± 60[d]
Methyl Salicylate	$C_8H_8O_3$	152	495.2–496.5[a]	33.5 ± 4.0[e]

[a] NIST chemistry webbook, [b] Leng et al. (2013), [c] Sigma Aldrich data sheet, [d] Nozière et al. (2001), [e] Karl et al. (2008).

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Table 4. Fractional oxidation of individual BVOC by ozone (F_{O_3}) and OH (F_{OH}) together with maximum literature reported acetone yields during ozonolysis (Y_{O_3}) and OH oxidation (Y_{OH}) taken to calculate maximum weighted average acetone yield (Atkinson and Arey, 2003).

BVOC	$\%_{total}$	F_{OH}	F_{O_3}	Y_{O_3}	Y_{OH}
α-pinene	24.5	0.38	0.62	0.08	0.15
β-pinene	19	0.82	0.18	0.07	0.13
Myrcene	14	0.36	0.64	0.29	0.45
Z-β-ocimene	25	0.34	0.66	0.24	0.2
E-β-ocimene	6.5	0.34	0.66	0.24	0.2
Limonene	11	0.44	0.56	0.02	0.03

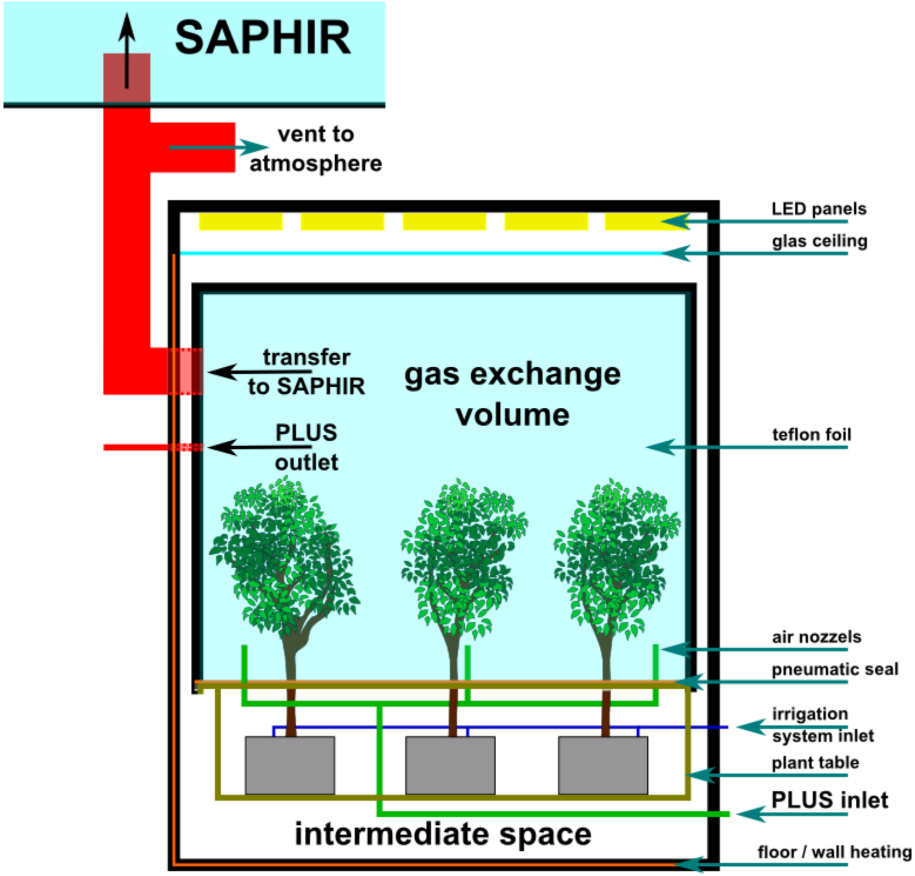

Figure 1. Schematic of the PLUS plant container. The green lines shows the inflow of synthetic air and other gases into PLUS (PLUS inlet) and the red line are the outflows of PLUS to either instrumentation (PLUS outlet), SAPHIR or the atmosphere.

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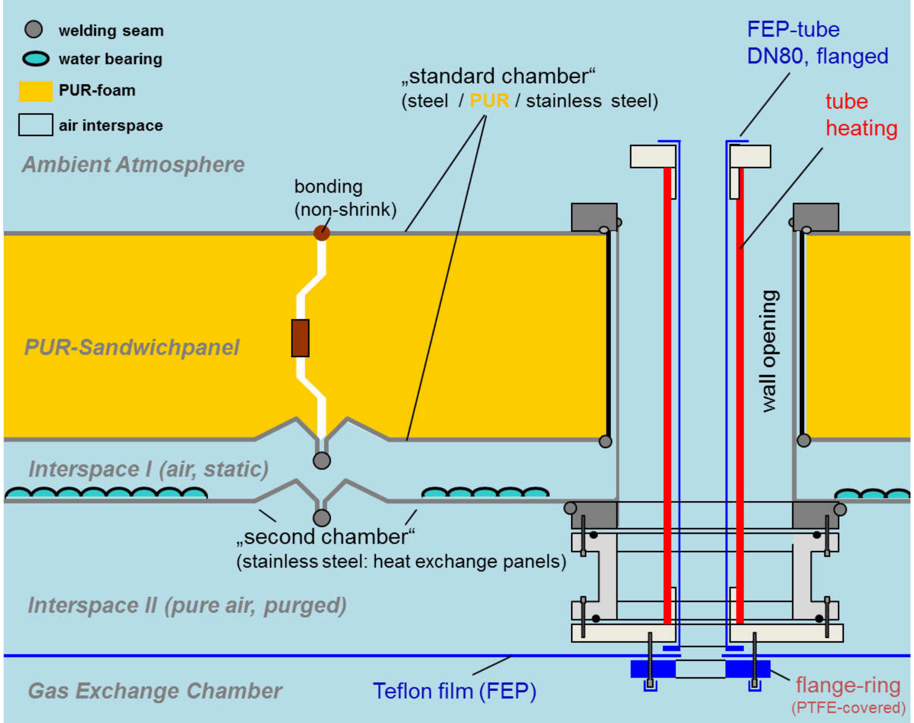

Figure 2. Horizontal (bird-eye) cut through the multi-layered walls of the triple-cage plant chamber system, including the double-walled wall opening and flanges for the transfer tube to SAPHIR.

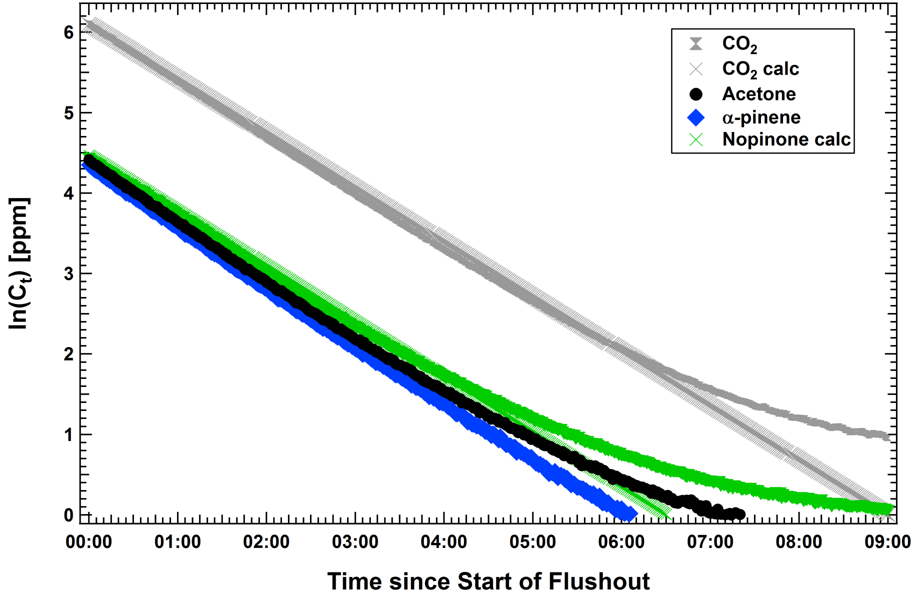

Figure 3. CO_2 and VOC flush out characteristic inside the PLUS gas exchange volume.

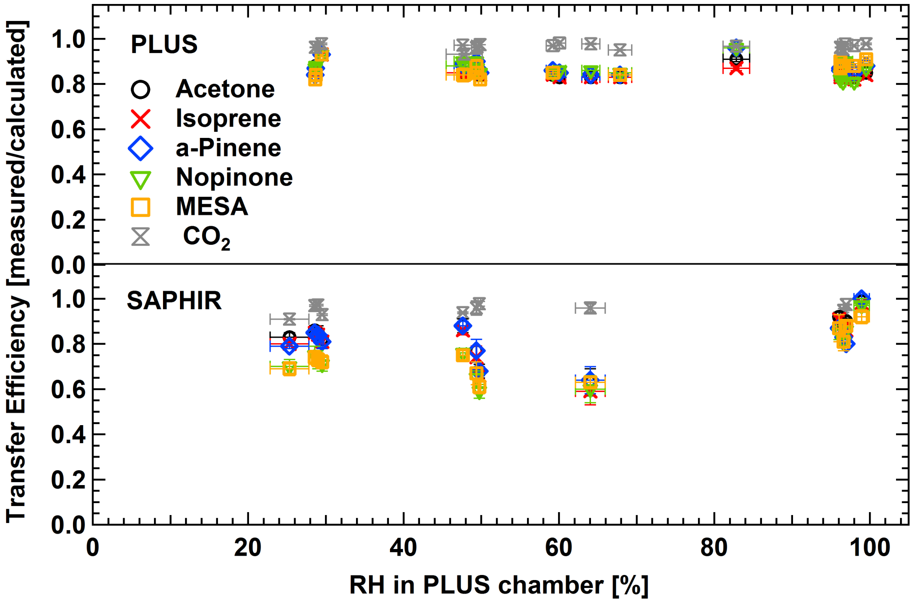

Figure 4. Measured/calculated averaged mixing ratios of VOC gas standard compounds. Upper panel shows the transfer efficiency between PLUS inlet and PLUS outlet. Lower panel shows the transfer efficiency between PLUS outlet and the SAPHIR chamber.

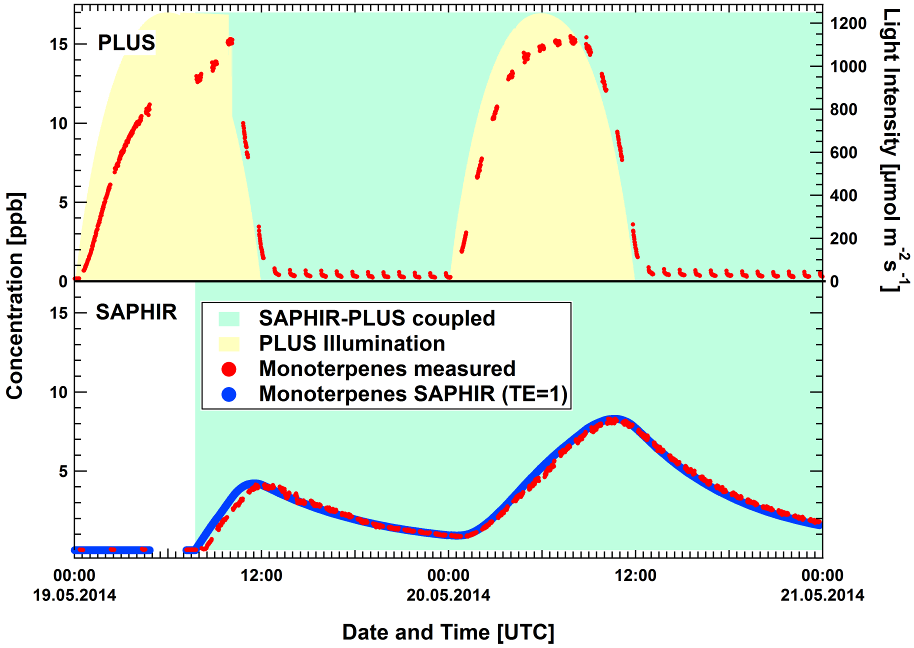

Figure 5. Illustration of monoterpene transfer from PLUS to SAPHIR when continuously coupling the chambers with a flow of 30 $m^3 h^{-1}$. Yellow shaded areas indicate time periods and intensity of light in the plant chamber, green shaded area indicates coupling of PLUS to SAPHIR.

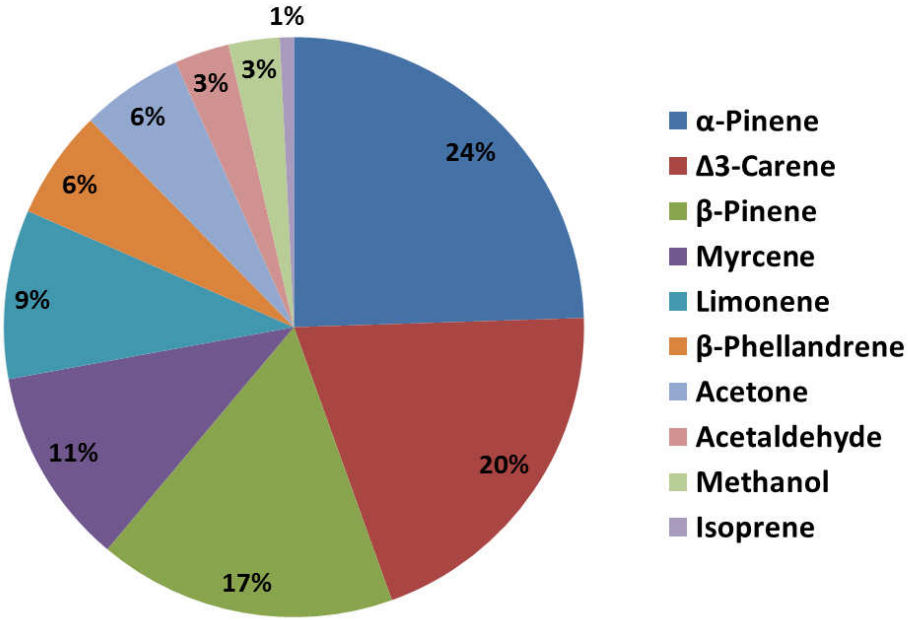

Figure 6. BVOC composition during the Temperature and Light dependency emission experiments using six *Quercus Ilex* trees. BVOC were measured with GC-MS/FID.

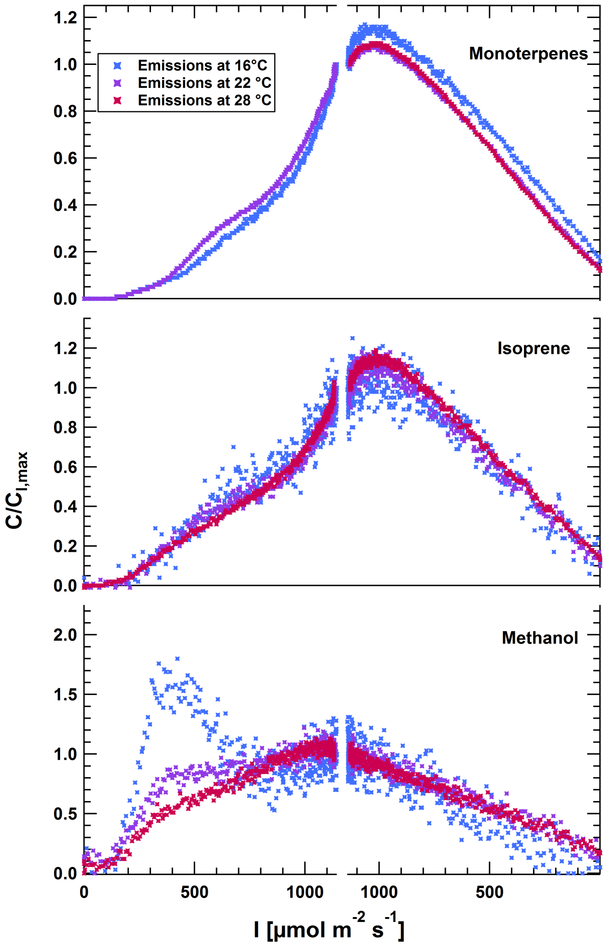

Figure 7. Light dependent emissions of *Quercus Ilex* under different temperature conditions with $C_{I,max}$ referring to observed concentrations at maximum light intensity (*I*) (upward branch).

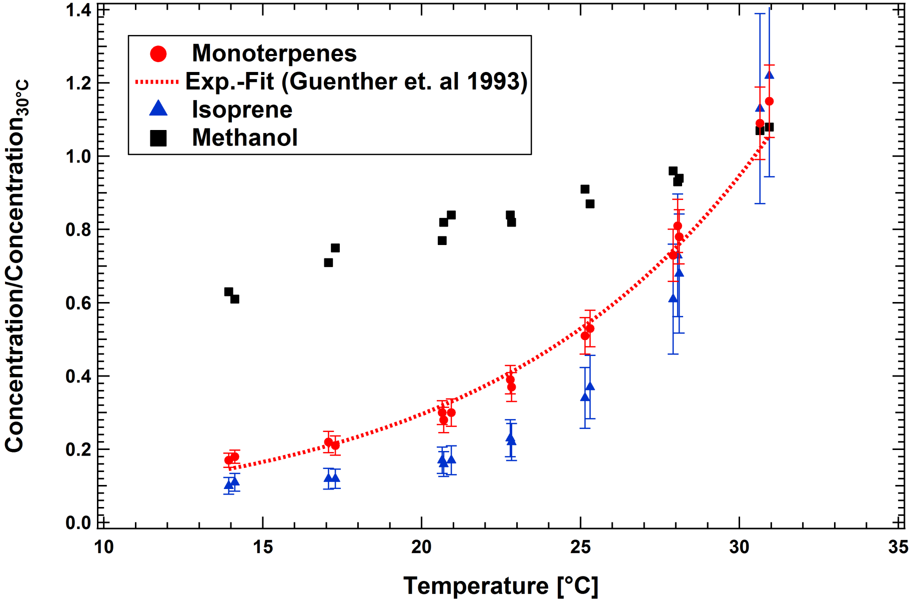

Figure 8. Temperature dependent emission of *Quercus Ilex*. One hour averaged data of peak emissions during the photoperiod are used.

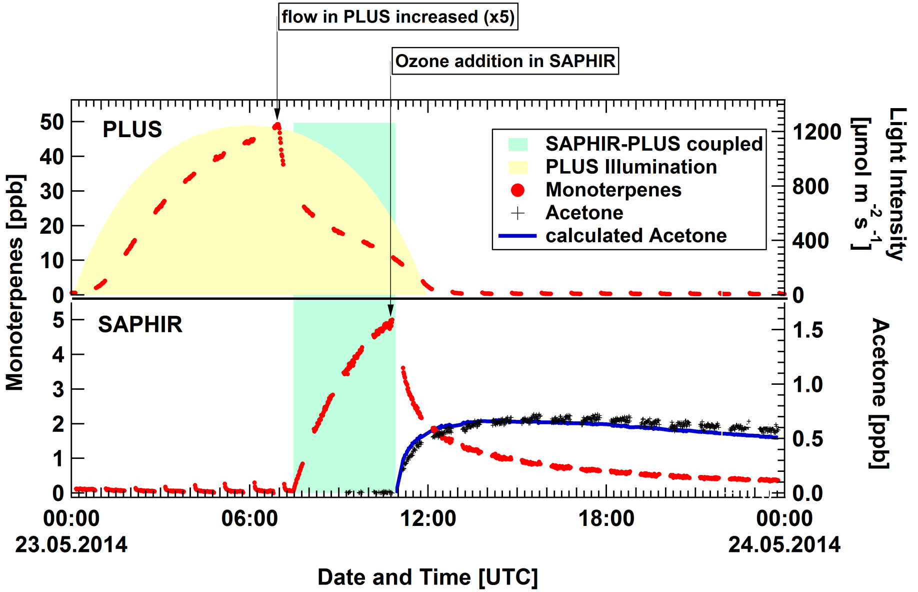

Figure 9. PLUS (upper panel) and SAPHIR (lower panel) observed concentrations of monoterpenes (red symbols) in an experiment performing a pulsed transfer of BVOC emissions. After ozone addition to the SAPHIR chamber, formation of oxidation products is observed. Acetone as one representative OVOC is shown as measured (black symbols) together with calculated Acetone (blue line).