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# A dynamic plant chamber system with downstream reaction chamber to study the effects of pollution on biogenic emissions

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# Abstract

A system of two dynamic plant chambers and a downstream reaction chamber has been set up to investigate the emission of biogenic volatile organic compounds (BVOC) and possible effects from pollutants such as ozone. The system can be used to compare BVOC emissions from two sets of differently treated plants, or to study the photo-

<sup>5</sup> pare BVOC emissions from two sets of differently treated plants, or to study the photochemistry of real plant emissions under polluted conditions without exposing the plants to pollutants. The main analytical tool is a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) which allows online monitoring of biogenic emissions and chemical degradation products. The identification of BVOCs and their oxidation products is aided by cryogenic trapping and subsequent in situ gas chromatographic analysis. The data presented in the paper demonstrates the good performance of the setup.

#### 1 Introduction

Volatile organic compounds (VOC) are reactive substances in the atmosphere which have a strong impact on atmospheric chemistry (Fehsenfeld et al., 1992; Riipinen et al., 2011; Sahu, 2012). Biogenic volatile organic compound (BVOC) emissions constitute approximately 90 % of global VOC emissions which are estimated to be 1150 Tg C yr<sup>-1</sup> (Guenther et al., 2006). Oxidation of BVOCs in the atmosphere in the presence of NO<sub>x</sub> leads to the formation of ozone. Tropospheric ozone is a greenhouse gas and a strong oxidant which makes it harmful for living organisms (Summerfelt and Hochheimer, 1997; Denman et al., 2007). Moreover, oxidation products of BVOCs contribute to secondary organic aerosol (SOA) formation through condensation on existing particles or the formation of new particles (Kulmala, 2003; Goldstein and Galbally, 2007). Aerosols and ozone can penetrate into the lungs of humans thus causing long- and

<sup>25</sup> have an impact on Earth's climate: ozone is a strong greenhouse gas and aerosols





short-term health effects (Harrison and Yin, 2000). Furthermore, aerosols and ozone

scatter and/or absorb solar radiation. Aerosols also influence the climate indirectly by serving as cloud-condensation nuclei (Andreae and Crutzen, 1997).

While BVOCs are known to affect the atmosphere and human health, much remains unknown about how atmospheric pollutants affect plant VOC emissions. Increased

- <sup>5</sup> ozone levels may increase or decrease BVOC emissions, depending on plant species and environmental conditions. For example, Beauchamp et al. (2005) showed that C6volatile emissions increased after ozone exposure in tobacco plants, while Hartikainen et al. (2012) showed decreased VOC emissions upon elevated ozone levels in birch trees. In addition, Karl et al. (2010) showed that pollutants like oxygenated VOCs can
- <sup>10</sup> be removed by plants through dry deposition. At the same time it is not understood how such deposition influences the ability of plants to emit BVOCs (Karl et al., 2010). Plant VOC emissions are affected by many environmental factors, including abiotic factors like temperature and light as well as biotic factors like herbivores, pathogens and neighboring plants (Niinements, 2010; Guenther et al., 2000; Sharkey and Loreto, 1993; Kegge and Pierik, 2010).

Here we present a setup of dynamic plant chambers and a reaction chamber, which can be used to study interactions between BVOC emissions and pollution. The main features include automated operation to study real plant emissions under different environmental conditions. BVOC analysis is based on proton-transfer-reaction time-of-flight

- <sup>20</sup> mass spectrometry (PTR-TOF-MS) which allows precise online measurements of different VOCs in the air with high mass resolution (Jordan et al., 2009; Graus et al., 2010). In addition, the PTR-TOF-MS is coupled to a gas chromatograph (GC) system in order to improve the identification of isomers (e.g. different monoterpenes). Results from an ozonolysis experiment with  $\beta$ -pinene and three experiments with birch (*Betula*
- <sup>25</sup> *pendula*) seedlings (referred to as experiment A, B, and C) are shown here to demonstrate the performance of the system.





#### 2 Description of the setup

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The schematic setup of the system is shown in Fig. 1. Two optional chamber setups are shown in charts A and B. Chart C shows how the PTR-TOF-MS is connected to the different sampling ports of the chamber system, and chart D shows the functioning of the GC system.

#### 2.1 The plant and reaction chambers system

As plant chambers we use two desiccators with a volume of 25 L each. The desiccators are identical and consist of three parts: the cap, the desiccator body and the hose, which is located in the cap. The hose has a long outlet (I = 25 cm, ID = 9 mm), which is directed towards the bottom of the desiccator and allows sampling from the center of the plant chamber. The gas inlet to the chamber is located at the top of the hose.

The custom-made reaction chamber is made from perfluoroalkoxy film (PFA, thickness 0.05 mm, HP Products, the Netherlands) and has a cylindrical shape. The walls were sealed by welding the PFA film with a heat gun (Steinel, Germany). The physical characteristics of the reaction chamber are the following: diameter = 45 cm, height = 50 cm, volume = 80 L. The bottom of the chamber is fixed to a ground plate covered with a PFA film. The axle of a polytetrafluoroethylene ventilator (PTFE, OD = 10 mm, Bola, Germany) is lead through the center of the ground plate, the ventilator is positioned in the center of the chamber. Operating the ventilator at 2 Hz keeps the cham-

<sup>20</sup> ber well mixed during the experiments. All mounting parts in contact with the air inside the reaction chamber were made from Teflon (PTFE). The tightness of the reaction chamber was tested by filling the chamber with acetone at levels of several hundred nmolmol<sup>-1</sup> and monitoring the mixing ratio without gas flow through the chamber. No significant leaks were detected.

<sup>25</sup> The flow through the plant chambers can be controlled by thermal mass-flow controllers (MKS Instruments, Germany) in the range 0–20 and 0–5 standard Lmin<sup>-1</sup> (standard is referring to standard conditions: 1013.25 hPa, 273.15 K) for chamber 1





and 2, respectively. During all experiments the flow through both plant chambers was  $2.5 \,L\,min^{-1}$ . We used pressurized (5 bars) ambient air which was purified through a custom made charcoal filter. The charcoal was cleaned once a week by removing the charcoal from the tube and placing it overnight in an oven at 160 °C.

- In the "dual plant chamber" setup (Fig. 1a) the sampling ports are located directly at the outlets of the plant chambers and a third sampling port is located after the charcoal filter to monitor the incoming air. In the "reaction chamber" setup (Fig. 1b) the sampling ports are located directly after the reaction chamber, after the plant chambers, and after the charcoal filter. Relative humidity and temperature sensors (HMP 60, Vaisala, Finland) are located at the outlets to monitor humidity and temperature in all chambers.
  - We used Teflon (PFA) tubing to connect the plant chambers, the reaction chamber, and instruments (length between plant and reaction chamber = 145 cm, ID = 9 mm). Defined amounts of ozone can be added before plant chamber 1 (Fig. 1a) or the reaction chamber (Fig. 1b) with an ozone generator (Model 49i-PS, Thermo Scientific, US).
- <sup>15</sup> This is done by turning on the generator (set to 1500 nmolmol<sup>-1</sup>) and switching valve 3. The ozone addition to the plant chamber 1 and the reaction chamber is controlled with a thermal mass-flow controller (MKS, Germany) in the range 0–2 L min<sup>-1</sup>. Ozone is monitored (O<sub>3</sub> analyzer model 49 W003 Thermo Environmental Instruments Inc., USA) at the outlet of either plant chamber 1 or the reaction chamber.
- <sup>20</sup> An array of nine 36W/840 TL-D lamps (Philips, the Netherlands) above the plant chambers is used to produce light levels of 130–150  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> photosynthetically active radiation (PAR:  $\lambda$  = 400–700 nm) at the center of the plant chambers when the lid was closed.

# 2.2 Analytical tools

### 25 2.2.1 PTR-TOF-MS

Figure 1c shows how the PTR-TOF-MS is switched between the three sampling ports of the chamber system, the effluent of the GC column (the PTR-TOF-MS is also used





as detector for the GC system), and laboratory air, which can be routinely monitored as well. This valve system is implemented with 1/8" PFA tubing, four 2-way and two 3-way Teflon (PFA) solenoid valves (TEQCOM, port size 1/8", orifice 0.125).

We use a standard PTR-TOF-MS (Ionicon Inc., Austria), which has been described

- <sup>5</sup> by Jordan et al. (2009), with the following parameters: temperature of the drift tube, 60 °C; temperature of the inlet tube, 60 °C; drift tube pressure, 2.15 hPa; ion source voltages, Us = 140 V, Uso = 92 V; E/N, 134 Td; extraction voltage at the end of the drift tube, Udx = 35 V. The ion source current is kept between 5 and 7 mA and we provide a water flow of 4 standard mLmin<sup>-1</sup> to the ion source. At the normal operational conditions the intensity of the primary signal (detected at m/z 21.023) is around 500–
- <sup>10</sup> conditions the intensity of the primary signal (detected at *m*/2 21.023) is around 500– 2000 cps. However, during the experiments B and C the primary signal was low (~ 100– 200 cps), whereas during experiment A the primary signal was at its normal level (~ 500 cps). During the ozonolysis of  $\beta$ -pinene experiment the primary signal was ~ 200 cps.

The settings of the TOF are such that every 60 microseconds a pulse of ions is injected into the mass spectrometer, which corresponds to a mass range of 0–1165 Th. 16667 of these initial mass spectra are averaged and saved to one mass scan which corresponds to a time resolution of one second. The mass resolution ( $m/\Delta m$ , where  $\Delta m$  is the full width at half maximum) is typically in the range of 3500–5000. Data processing is done with Interactive Data Language (IDL, version 7.0.0, ITT Visual Infor-20 mation Solutions), using custom made routines described by Holzinger et al. (2010a).

Mixing ratios of most compounds were calculated according to the method described in Holzinger et al. (2010b), which involves the use of default reaction rate constants (3×10<sup>-9</sup> cm<sup>3</sup> s<sup>-1</sup> molecule<sup>-1</sup>), default transmission efficiencies, and calculated reaction times. The accuracy of the calculated mixing ratios should be better than 50 % for most compounds (Holzinger et al., 2010b). In addition, gas standards were used to calibrate the mixing ratios of monoterpenes, acetaldehyde and acetone with an accuracy of 17%, calculated as the sum of the precision of PTR-TOF-MS and the accuracy of the gravimetrically mixed calibration standard.





The mixing ratios of monoterpenes were calculated as the sum of the signals detected at m/z 81.069 and m/z 137.133 for experiments with pure compounds (here  $\beta$ -pinene). However, we found that in experiments with biogenic emissions other compounds were also detected at m/z 81.069 (C6 alcohols or aldehydes). Calibration experiments with a gas standard containing  $\alpha$ -pinene showed that 32% of the total amount of the monoterpene was found at m/z 137.133. Thus, for the experiments with biogenic emissions, mixing ratios of monoterpenes were calculated by multiplying the signal detected at m/z 137.133 by a calibration factor of 3.13.

# 2.2.2 GC system with VOCs cryogenic trapping

- <sup>10</sup> The GC system features two cryogenic traps that can be electrically heated with resistance wire and submerged into liquid nitrogen by pneumatic lifters. The sampling line (1/8" PFA) is connected (port 1 in Fig. 1c and d) downstream the two 3-way valves that connect the PTR-TOF-MS to the sampling ports of the chamber system. This ensures that GC-sampling and online monitoring with the PTR-TOF-MS occurs
- at the same time. The primary sampling trap is a W-shaped 1/8" stainless steel tube (ID = 1.5 mm) with sulfinert coating (Restek Inc.) which is connected with 1/16" PEEK tubing to a 6-port stainless steel Valco valve (sulfinert coating). A needle valve before the trap is used to regulate the sampling flow and ensures that sampling is at low pressure (~ 200 hPa) to prevent condensation of oxygen. The collection efficiency has been
- tested for  $\alpha$ -pinene, methanol and toluene to be close to 100 % for sampling flows up to 35 mLmin<sup>-1</sup>. During operation the trap is pre-cooled for 5 min before sampling. We use a standard sampling flow of 30 mLmin<sup>-1</sup> which is measured with a thermal mass-flow meter (MKS Instruments, Germany) and maintained with a membrane pump (Vacu-ubrand GmbH, Germany) downstream of the sampling trap.
- <sup>25</sup> Switching the 6-port valve allows transferring the sample to the focusing trap, which consists of a U-shape 1/8" stainless steel tube with a glass capillary through it (ID =  $320 \,\mu\text{m}$ , SGE Analytical Science, Australia). The sample is released by heating the sampling trap to  $100^{\circ}\text{C}$  within 2 min. A helium flow (ultrapure He, air products) of 2





standard mL min<sup>-1</sup> is used to transfer the sample to the focusing trap. Typically a period of 10 min is allowed to complete the transfer, which corresponds to a gas volume 5 times the internal volume of the sampling trap, the focusing trap and the transfer lines. Immediately thereafter the sample is injected into the GC column while the effluent is monitored with the PTR-TOF-MS. Injection is achieved by heating the focusing trap to 200°C within 75 s.

For the chromatography we use a 30 m DB-5MS column (ID = 0.25 mm, film thickness =  $0.25 \,\mu\text{m}$ ) with He as a carrier gas (2 standard mLmin<sup>-1</sup>, controlled with 20 standard mLmin<sup>-1</sup> thermal mass-flow controller, MKS Instruments, Germany). After injection the column is kept at 40 °C for one minute, heated to 150 °C at 5 °C min<sup>-1</sup> and then to 250 °C at 20 °C min<sup>-1</sup>.

For analysis the effluent of the GC column is diluted with 38 mL of nitrogen (ultrapure nitrogen, 5.7 purity, air products), which is achieved by providing excess nitrogen and setting the flow into the PTR-TOF-MS to 40 standard mLmin<sup>-1</sup> (Fig. 1d). The mixture of effluent and nitrogen is transferred through 1/8'' PFA line to port 6 (Fig. 1c and d).

### 2.3 Automation and control system

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Valve positions, flows, cryotrap positions, temperatures and other elements are automatically operated with a controlling set (National Instruments NI cDAQ-9178) that can be programmed in Labview's (LabVIEW 2011, National Instruments) user-friendly interface. Control sequences are created as simple text documents containing the commands for valve positions, set temperatures, etc.

The values of the elements underlined red in Fig. 1 are saved to an engineering log together with other parameters such as time, ozone mixing ratios in the reaction chamber, set value of ozone generator, sampling and focusing cryotrap temperatures,

<sup>25</sup> and temperature in the GC oven. These data are recorded every second to fit the time resolution of the PTR-TOF-MS.





### 2.4 Operation of the system

To demonstrate the operation of the system, Fig. 2 shows the course of the mixing ratios detected at m/z 81.069 (C<sub>6</sub>H<sub>9</sub><sup>+</sup> fragment) for one cycle of experiment A. The PTR-TOF-MS was switched between the different ports to measure as follows (see

- Fig. 2): for 10 min reaction chamber air, for 5 min purified air, for 10 min plant chambers air, for 25.5 min GC effluent, for 10 min plant chambers air, for 36 min reaction chamber air (ozone addition to the reaction chamber happens during this period), for 25.5 min GC effluent, for 5 min lab air. Thereafter, new two-hour cycles were started automatically.
- <sup>10</sup> The periods of GC sampling (7 min each) are also indicated in Fig. 2. Ozone addition lasted for 17 min (see blue bracket in Fig. 2) and GC sampling was performed during the last 7 min of the ozone treatment.

The following periods (indicated in Fig. 2 by the respective lines below the *x* axis) were used for averaging/integration: last 7 min of non-ozonated reaction chamber air <sup>5</sup> measurements, last 4 min of purified air measurements, last 9 min of first plant chamber air measurements, first 15 min of first GC chromatogram, last 4 min of second plant chamber air measurements, last 7 min of ozonated reaction chamber air measurements, first 15 min of context of the second plant chamber air measurements, last 7 min of ozonated reaction chamber air measurements, first 15 min of context of the second plant chamber air measurements, last 7 min of ozonated reaction chamber air measurements, first 15 min of second GC chromatogram.

### 2.5 Experiments performed

#### 20 2.5.1 Ozonolysis of $\beta$ -pinene

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During this experiment flow through the reaction chamber was maintained at  $7 \text{ Lmin}^{-1}$  by two flow controllers which were set to 5 and  $2 \text{ Lmin}^{-1}$ , respectively. This resulted in an air residence time of 11.5 min in the reaction chamber. The larger flow contained ~ 350 nmol mol<sup>-1</sup> of  $\beta$ -pinene, which was produced by diluting a small flow (20 mLmin<sup>-1</sup>) of headspace air from a flask with liquid  $\beta$ -pinene (Sigma Aldrich, 99%) into the larger





flow of purified air. Ozone levels of  $\sim 1.3 \,\mu\text{mol\,mol}^{-1}$  were produced in the 2 L flow by the ozone generator.

# 2.5.2 Birch seedling experiments

Experiment A was performed on 4-5 August 2012, experiment B - on 22-23 Au-

- <sup>5</sup> gust 2012 and experiment C on 24–25 August 2012. Birch (*Betula pendula*) seedlings were collected with their surrounding sandy soil from a forest close to the Utrecht University campus 1–2 days before the experiments, and placed in 250 mL pots. The seedlings were 1–2 yr old. Due to weather conditions, the soil of seedlings used in experiment C was very dry. After transfer to the lab, the seedlings were placed next to the to the lab.
- <sup>10</sup> plant chambers, where the TL-D lamps produced light levels of 130–150  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> PAR with a light period from 07:00 till 23:00 LT (16 h light, 8 h dark). Day and night temperatures were 21.5 ± 0.2 and 20.2 ± 0.2 °C, respectively. Relative humidity was 40– 60 %. Three plants were put into each plant chamber. After the lids were closed the air flow of 2.5 L min<sup>-1</sup> was maintained for 30 min before the start of the experiment to allow plant emissions to stabilize.

After the experiment, leaves were harvested, fresh weight was measured and leaf area was determined with a Li-3100 Area Meter (Lincoln, Nebraska, USA). Dry weight was measured after placing the leaves in an oven at 70 °C for at least 48 h.

Before experiments B and C, the reaction chamber was pre-cleaned overnight by <sup>20</sup> being flushed with purified air containing ozone mixing ratios of ~ 430 nmol mol<sup>-1</sup>. To check if chambers were clean, background measurements (with purified air) of empty plant and reaction chambers were made. The experiments were performed according to the measurement cycle described in Sect. 2.4.

Emission rates (ER) of the birch seedlings were calculated according to Eq. (1):

$$_{25} \quad \mathsf{ER} = \frac{[\mathsf{VOC}] \cdot M_{\mathsf{VOC}} \cdot F_{\mathsf{cham}}}{\mathsf{DW}}$$



(1)

where [VOC] is the mixing ratio (in nmol mol<sup>-1</sup>, with subtracted background) and  $M_{\rm VOC}$ is the molecular weight (in  $gmol^{-1}$ ) of the compound under consideration,  $F_{cham}$  is the air flow through the plant chambers in mol  $h^{-1}$ , and DW is the leaf dry weight of the measured plants in q. The resulting emission rate has the unit of  $nqq(DW)^{-1}h^{-1}$ .

- The mixing ratios of the corresponding species in the purified air supplied into the 5 plant chambers were used as a background and subtracted from the data. All three experiments were used to calculate emission rates during the day (from the start of the experiment till 10 p.m. and from 9 a.m. till the end of the experiment) and night (from 12 p.m. till 6 a.m.).
- Ozonolysis of the birch seedling emissions was performed by ozone additions into 10 the reaction chamber (see Sect. 2.4). Yields of the ozonolysis products were calculated according to Eq. (2):

yield= $\frac{[product]_{after} - [product]_{0}}{[monoterpenes]_{0} - [monoterpenes]_{after}}$ 

where  $[product]_{after}$  and  $[product]_0$  are the mixing ratios (in nmolmol<sup>-1</sup>) of the product after and before the ozone addition, and [monoterpenes]<sub>after</sub> and [monoterpenes]<sub>0</sub> the mixing ratios (in  $nmolmol^{-1}$ ) of monoterpenes after and before ozone addition, respectively.

#### System performance 2.6

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Figure 3 presents online data (experiment B) of the plant chambers and the reaction chamber without ozone addition. In general, there is good agreement between the mixing ratios in the reaction chamber and the plant chambers for most compounds. However, for monoterpene and m/z 85.064 the mixing ratios were somewhat lower in the reaction chamber compared to the plant chamber. This is likely caused by the more sticky nature of monoterpenes and the compound detected at m/z 85.064. For

(2)

m/z 69.070 and 71.049 in some cases lower mixing ratios were observed in the plant chambers. This might be caused by contamination from the reaction chamber walls.

Example chromatograms obtained during experiment A are shown in Fig. 4. The chromatogram obtained from the non-ozonated reaction chamber experiment shows

- <sup>5</sup> three major monoterpene (m/z 137.133) peaks (Fig. 4d, at 472, 601, and 681 s). These peaks are also present at m/z 81.069 (Fig. 4c). The chromatogram of m/z 81.069 shows that the signal at m/z 81.069 cannot be entirely attributed to monoterpenes because two additional peaks (Fig. 4c, at 292 and 379 s) show up which are inconsistent with C<sub>10</sub>-compounds. The second peak at m/z 81.069 (at 379 s) was attributed to
- <sup>10</sup> a fragment of  $C_6H_{10}O$  because a peak with the same retention time was observed at m/z 99.081 ( $C_6H_{11}O^+$ ). Fall et al. (1999) report biogenic emission of 2-hexenal which likely corresponds to the observed second peak at m/z 81.069 based on its position in the chromatogram and the known retention index of it (Goodner, 2008). The first peak at m/z 81.069 was observed simultaneously with a peak at m/z 83.085 (corresponds to a molecular formula  $C_6H_{10}$ ) and m/z 101.095 (corresponds to a molecular formula
- $C_6H_{12}O$ ) which indicates that this peak likely corresponds to a hexanal or hexenol (Fall et al., 1999).

Previous studies (Konig et al., 1995) showed that birch (*Betula pendula*) emits  $\alpha$ pinene, d-limonene,  $\beta$ -phellandrene and sabinene. Based on the performed calibration <sup>20</sup> measurements the monoterpene peaks were identified as  $\alpha$ -pinene, d-limonene and, possibly,  $\beta$ -phellandrene. For  $\beta$ -phellandrene no calibration standard was available, but the relative position of the corresponding peak in the chromatogram and the known retention indices of the emitted monoterpenes (Goodner, 2008) led to the conclusion that this peak corresponds to  $\beta$ -phellandrene. The chromatogram of sampled purified air

<sup>25</sup> (background) confirmed that there were no peaks interfering with the proper detection of monoterpenes. Two little peaks observed after  $\alpha$ -pinene and d-limonene were not identified.

A crucial point of the GC/PTR-TOF-MS system is the quantitative correspondence between GC and online measurements. Equation (3) defines the recovery factor (RF)





as the ratio between the amount of substance of a VOC measured with the GC setup  $(n(VOC)_{GC})$  vs. the amount of substance sampled  $(n(VOC)_{sampled})$ . The former was calculated by integrating the GC peak(s) at a particular m/z value, the latter was calculated from the online measured mixing ratio at the same m/z during the time of sampling and the sampled volume:

 $RF = n(VOC)_{GC}/n(VOC)_{sampled}$ .

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In Table 1 we present recovery factors of several compounds based on experiments A, B and C. To calculate the recovery factors no background was subtracted from the measured signal. The obtained recovery factors are in the range 0.71–1.38 indicating a reasonable agreement between online and GC measurements. Deviations from 1 are most likely due to different levels of instrumental background during the online and GC effluent measurements. Also, there might be an overestimation of compound mixing ratios in nitrogen-based GC effluent vs. air-based online measurements.

### 2.7 Data filtering and statistics

<sup>15</sup> For all performed analyses we considered ions above m/z 40, and ions detected at m/z 31.018 (CH<sub>3</sub>O<sup>+</sup>) and m/z 33.033 (CH<sub>5</sub>O<sup>+</sup>). In order to identify plant emissions and ozonolysis products we applied a Student's *t* test (Coladarci, 2010; LeBlanc, 2004) on the sets of data to be compared (e.g. mixing ratios in air entering the plant chamber vs. mixing ratios in the plant chamber; or mixing ratios in the reaction chamber with and without ozone, respectively). The Student's *t* test returns a significance parameter, *p*, that indicates the probability that the two datasets are not different. As threshold we used *p* = 0.05 indicating a 95 % probability that the datasets are significantly different. The T-statistic parameter indicates the difference between the means of the two datasets (normalized by the variance). As threshold for the T-statistic parameter we used 10, 2.8 and 3 for  $\beta$ -pinene ozonolysis, birch emissions, and ozonolysis of birch emissions, respectively.



(3)



Contamination of the chamber walls was an issue for both sets of experiments, the ozonolysis of  $\beta$ -pinene and birch emission. Therefore we applied additional filters to these data sets. For the  $\beta$ -pinene experiment we rejected all species the yield of which was below 0.25%. For the ozonolysis of birch emissions the following two criteria had to be satisfied: (a) the night time yield had to be smaller than the yield during the following day; (b) the change in the mixing ratio upon ozonolysis had to be above 27 pmol mol<sup>-1</sup> (which corresponds to the detection limit of PTR-TOF-MS). The latter filter was also applied in order to select the ions which were significantly emitted by the birch seedlings.

#### 10 3 Results and discussion

# 3.1 Ozonolysis of $\beta$ -pinene

In order to test the functionality of the reaction chamber we performed an ozonolysis experiment with  $\beta$ -pinene, a reaction that has been widely studied (Lee et al., 2006; Jaoui and Kamens, 2003; Arey et al., 1990). Figure 5 shows the course of  $\beta$ -pinene, some oxidation products, and the ozone mixing ratios. After ~ 1 h of adding ozone to the reaction chamber,  $\beta$ -pinene and ozone mixing ratios in the reaction chamber reached equilibrium: [ $\beta$ -pinene] ~ 220 nmol mol<sup>-1</sup> and [O<sub>3</sub>] ~ 340 nmol mol<sup>-1</sup>.

Among the oxidation products of  $\beta$ -pinene, we observed formaldehyde (detected as CH<sub>3</sub>O<sup>+</sup>, *m/z* 31.018), acetone (detected as C<sub>3</sub>H<sub>7</sub>O<sup>+</sup>, *m/z* 59.049) and nopinone <sup>20</sup> (detected as C<sub>9</sub>H<sub>15</sub>O<sup>+</sup>, *m/z* 139.112 and fragmented as C<sub>9</sub>H<sup>+</sup><sub>13</sub>, *m/z* 121.102). The yields of all observed oxidation products are presented and compared to the yields from literature in Table 2. The comparison indicated that the yields obtained in this study are somewhat lower (except acetone) but comparable to the yields described in the literature. The lower yields were potentially caused by (i) the shorter residence time of air in the reaction chamber (11.5 min) in comparison with other studies, (ii) lower





 $\beta$ -pinene and ozone mixing ratios, and/or (iii) the absence of an OH scavenger which would lead to a longer time for the system to reach equilibrium.

In addition to known compounds, several other compounds were observed, which had not been described previously. For the single experiment reported here we cannot

- <sup>5</sup> exclude the possibility that these products were artifacts from wall contamination. Nevertheless, these newly observed compounds show the potential of the setup to identify more products of the oxidation of  $\beta$ -pinene, when improved cleaning protocols are followed and background measurements are performed. Finally, we observed that mixing ratios of sticky compounds like formic acid (*m*/*z* 47.013) increased slower in the reac-
- tion chamber than other compounds (Fig. 5), indicating that a fraction of these products are lost to the walls of the reaction chamber. However, the loss is limited and towards the end of the experiment (~ 300 min, Fig. 5) the gas phase levels of m/z 47.013 were in equilibrium.

# 3.2 Emission rates of birch seedlings

- In each experiment, the plants in the plant chambers had a total dry weight of 4.1–5.3 g, and a total leaf area of 1296–1413 cm<sup>2</sup>. All reported compounds were emitted during the day and many of them during the night, with daytime emissions being 1.8–3.2 times higher than nighttime emissions (Table 3). Increased emissions of BVOCs during the day and upon exposure to increased light intensity were reported before
  in several plant species including lima bean, cotton and poplar (Loughrin et al., 1994; Loivamöki et al., 2007; Arimura et al., 2008). A broad spectrum of the amitted com-
- Loivamäki et al., 2007; Arimura et al., 2008). A broad spectrum of the emitted compounds was observed indicating the good sensitivity of the system even towards the compounds emitted in low quantities during the day as well as during the night. For several compounds emitted during the day no emissions at night were observed.





#### 3.3 Ozonolysis of birch emissions

Figure 6 shows the course of the measured ozone and monoterpene mixing ratios. Minimum monoterpene mixing ratios and maximum ozone mixing ratios were observed at the same time in the reaction chamber demonstrating that chemical reactions with

- ozone were the cause of monoterpenes depletion (Atkinson and Arey, 2003). We modeled the monoterpene mixing ratios in the reaction chamber during the period shown in Fig. 6 in order to check if the degradation rate of monoterpenes was in agreement with the measured ozonolysis rate constants of the observed monoterpenes emitted from the birch seedlings. The initial monoterpenes mixing ratio, the mixing ratio of ozone,
- and first order kinetics were used. The initial monoterpenes mixing ratio was attributed to individual monoterpenes by using the information from the chromatogram shown in Fig. 4d. The relative fractions were 0.28, 0.47, and 0.25 for  $\alpha$ -pinene, d-limonene, and  $\beta$ -phellandrene, respectively. The reaction rates for these compounds with ozone have been measured to be 8.7 × 10<sup>-17</sup>, 2.0 × 10<sup>-16</sup> and 4.8 × 10<sup>-17</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, respec-
- tively (Atkinson, 1997; Shorees et al., 1991). Using this information the degradation of the monoterpenes was calculated separately and the total monoterpene mixing ratio at every time step was calculated as the sum of the individual contributions. The measured and modeled monoterpene mixing ratios (see Fig. 6) agree reasonably well, showing that the general description of the observed chemistry in the reaction cham-
- <sup>20</sup> ber is adequate. Somewhat lower measured monoterpene mixing ratios in comparison to the calculated values were associated with the absence of an OH scavenger in the system which could lead to a faster monoterpene degradation due to reactions with the OH radical.

Figure 7 shows averaged monoterpene mixing ratios measured online in the reaction chamber before and after ozone addition in experiment B. The decrease of monoterpene signal during/after ozonolysis as shown in Fig. 6 and described above was well reproducible. Due to the low primary signal the sensitivity of the instrument during experiment B was rather low which caused the detection of only few ions produced during





the ozonolysis. Despite the reasonable understanding of the chemistry happening in the reaction chamber it was difficult to identify ozonolysis products from experiments A–C. The reaction chamber was not well cleaned before the start of experiment A and ozonolysis products were also from contamination, i.e. reactive organic species stick-

- <sup>5</sup> ing to the walls of the reaction chamber system. For example, during experiment A the production of m/z 61.029 (calculated as a difference in mixing ratios for an ion in the reaction chamber with and without ozone added) during the night was higher than during the following day, despite much lower monoterpene levels during the night. This indicated a significant contribution from contamination to the signal of the ion, and in
- experiment A a similar behavior was observed for many other ions. In the experiments B and C the proper cleaning procedure was applied, therefore the abovementioned problems were not encountered. The change in monoterpenes mixing ratio upon the ozone addition was below the detection limit of PTR-TOF-MS due to very low plant emissions in experiment C. Therefore, it was not possible to calculate the yields for experiment C and apply the filter (a) described in Sect. 2.7.

In order to overcome these issues the filters mentioned in Sect. 2.7 were developed. Initially we detected 193 ions during experiments A, B and C. Of these, 43 and 60 ions passed the Student's *t* test in experiment A and B, respectively. None of the 43 ions from experiment A and only 2 ions from the 60 ions from experiment B passed the additional filters (a) and (b) m/r = 47,049 (corresponding to the melagular formula C  $H = 0^+$ )

tional filters (a) and (b): m/z 47.048 (corresponding to the molecular formula  $C_2H_7O^+$ ) with a molar yield 25.9±9.8% and m/z 73.029 (corresponding to the molecular formula  $C_3H_5O_2^+$ ) with a molar yield 29.5±8.2%.

Despite the low number of detected ozonolysis products, the above mentioned experiments demonstrated the capability of the system to detect ozonolysis products even

<sup>25</sup> at low mixing ratios of the parent compounds which can be improved by better reaction chamber pre-cleaning protocols and better (standard) PTR-TOF-MS performance, in which case the number of ions removed by filters (a) and (b) would be much reduced.





### 4 Conclusions

The setup to measure impact of pollution on plant emissions was tested and first results are reported here. In the  $\beta$ -pinene ozonolysis experiment the expected products were observed, although with somewhat lower yields than described in the literature. In the

- <sup>5</sup> experiments with real plant emissions, mixing ratios in the plant chambers and the reaction chamber are shown to coincide, showing good quantitative transfer of the VOCs between these components of the setup. This shows a good performance of the plant chamber and the reaction chamber setup, including ozone addition and online VOC measurements.
- <sup>10</sup> The sampling efficiency of the GC system has been tested. The recovery factors were within the range of 0.71–1.38, indicating that cryogenic sampling and the transfer through the GC system is adequate. The added value of the GC part of the system was clear from the analysis of birch seedling emissions, where it allowed us to distinguish three specific monoterpenes within the birch monoterpene emissions.
- We performed experiments with birch seedlings and found emission of 14 species. As expected, birch emission rates were higher during the day than during the night (1.8–3.2 fold higher), and for several of these species no nighttime emissions could be detected.

Addition of ozone to the birch seedling emissions resulted in decreased monoter-<sup>20</sup> pene mixing ratios. The modeled monoterpene mixing ratios in the reaction chamber agreed reasonably well with the measured levels. Our results show that our setup is capable of detecting ozonolysis products at low levels (< 1 nmol mol<sup>-1</sup>) of biogenic emissions, although relatively few ozonolysis products were observed. Comparison of experiment A with B and C shows that proper cleaning protocols are essential.

<sup>25</sup> The flexibility of the setup provides the possibility to perform a broad spectrum of experiments. The full automatization of the system allows easy-to-perform long- and short-term measurements. Therefore, the presented setup is a valuable tool to study the effects of pollution on plant emissions.





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A dynamic plant chamber system with downstream reaction chamber

J. Timkovsky et al.



Table 1. Recovery factors (RF) for several compounds, calculated from experiment A, B and
C using Eq. (3). All chromatograms that sampled from the ozone free reaction chamber have
been included into this analysis ( $n = 40$ ). Numbers shown are averages $\pm$ SD.

Compound or $m/z$	Formula $H^+$	$RF \pm SD$
33.033	$CH_4OH^+$	$0.75 \pm 0.10$
43.018	$C_2H_3O^+$	$0.82 \pm 0.07$
59.049	$C_3H_7O^+$	$0.71 \pm 0.08$
61.029	$C_2H_5O_2^+$	$1.38 \pm 0.26$
69.07	$C_5H_9^+$	$1.09 \pm 0.28$
87.045	$C_4H_7O_2^+$	$1.10 \pm 0.16$
87.081	$C_5H_{11}O^+$	$1.20 \pm 0.25$
monoterpenes	C <sub>10</sub> H <sup>+</sup> <sub>17</sub>	$1.23 \pm 0.31$





**Table 2.** Molar yields of ozonolysis products of  $\beta$ -pinene obtained in this study and in the literature (Lee et al., 2006<sup>a</sup>; Arey et al., 1990<sup>b</sup>; Hatakeyama et al., 1991<sup>c</sup>; Jaoui and Kamens, 2003<sup>d</sup>; Larsen et al., 2001<sup>e</sup>; Orlando et al., 2000<sup>f</sup>; Wisthaler et al., 2001<sup>g</sup>).

Product	m/z	Formula $H^+$	Yield, % [literature]	Yield, % [this work]
formaldehyde	31.018	CH₃O <sup>+</sup>	23 <sup>e</sup> –54 <sup>c</sup>	5.9
	33.033	$CH_4OH^+$		0.35
	41.038	$C_3H_5^+$		0.53
	43.018	$C_2H_3O^+$		4.17
acetaldehyde	45.033	C <sub>2</sub> H <sub>4</sub> O	0.6 <sup>a</sup>	1.07
formic acid	47.013	$HCOOH_2^+$	2.0 <sup>f</sup> –38.0 <sup>e</sup>	1.76
	47.022	no match		0.42
acetone	59.049	$C_3H_7O^+$	2.0 <sup>f</sup> –16.0 <sup>g</sup>	16.90
acetic acid	61.029	$C_2H_5O_2^+$	1.4 <sup>a</sup>	0.98
	73.029	$C_3H_5O_2^{\mp}$		0.28
	83.050	$C_5H_7O^+$		1.81
	95.050	$C_6H_7O^+$		0.67
	107.085	C <sub>8</sub> H <sup>+</sup>		0.26
	109.065	C <sub>7</sub> H <sub>9</sub> O⁺		0.36
	109.101	C <sub>8</sub> H <sup>+</sup> <sub>13</sub>		0.43
nopinone	121.102; 139.112	$C_9H_{15}O^+$	15 <sup>ª</sup> –79 <sup>°</sup>	6.5
	139.137	C <sub>10</sub> H <sup>+</sup> <sub>19</sub>		1.23
	140.114	no match		0.54
m153	153.092	$C_9H_{13}O_2^+$	1.9 <sup>d</sup> –2.8 <sup>a</sup>	0.35
m155	155.105	$C_9H_{15}O_2^+$	0.8 <sup>a</sup> –5.3 <sup>d</sup>	0.51
m185	185.115	$C_{10}H_{17}O_{3}^{+}$	0.1 <sup>a</sup> -0.5 <sup>d</sup>	0.26





**Table 3.** Average night and day emission rates of birch seedlings. Daytime light levels were  $130-150 \,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$  PAR. Day and night temperatures were  $21.5 \pm 0.2$  and  $20.2 \pm 0.2$  °C, respectively; "–" corresponds to no emission at night.

Compound or <i>m/z</i>	Formula H <sup>+</sup>	Night emissions, $ngh^{-1}g^{-1} \pm SD$	Day emissions, $ngh^{-1}g^{-1} \pm SD$
41.038	$C_3H_5^+$	$15.3 \pm 5.4$	$28.1 \pm 6.7$
43.018	$C_2H_3O^+$	27.6 ± 10.4	61.0 ± 15.7
43.054	$\overline{C_3H_7^+}$	$6.0 \pm 2.6$	$12.5 \pm 2.9$
45.033	$C_2H_5O^+$	$65.9 \pm 28.6$	$150.9 \pm 46.2$
59.049	$C_3H_7O^+$	91.7 ± 19.5	$192.5 \pm 52.6$
61.029	$C_2H_5O_2^+$	$12.2 \pm 11.0$	23.7 ± 13.1
63.044	$C_2H_7O_2^{\mp}$	$3.7 \pm 3.3$	$7.3 \pm 3.6$
69.070	$C_{5}H_{9}^{+}$	-	$10.7 \pm 5.7$
71.049	$C_4H_7O^+$	$12.3 \pm 5.6$	$39.5 \pm 20.6$
71.085	$C_5H_{11}^+$	-	$5.8 \pm 2.3$
85.064	$C_5H_9O^+$	-	$19.4 \pm 8.4$
87.045	$C_4H_7O_2^+$	-	$9.1 \pm 2.8$
87.081	$C_5H_{11}O^+$	-	$8.8 \pm 3.3$
monoterpenes	$C_{10}H_{17}^{+}$	$30.7 \pm 40.4$	$93.9 \pm 72.0$



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**Fig. 1.** Schematic overview of the setup with two optional chamber configurations (**A** and **B**), PTR-TOF-MS connections (**C**) and GC sampling system (**D**). Port numbers 2, 3 and 4 indicate the sampling positions for the PTR-TOF-MS. The GC samples through port 1 and the GC-effluent is analyzed with the PTR-TOF-MS through port 6. Lab air is analyzed through port 7 and port 5 connects the GC system to purified air for cleaning. The following abbreviations were used: NV – needle valve, PC1, PC2 – plant chambers; RC – reaction chamber, GC – gas chromatograph; V1-V5 and V7-V9 – 2-way (circles) and 3-way (triangles) valves, V6 is a 6-port Valco valve; F1, F2, F3, F4 – flow controllers; RH1, RH2, T1, T2 – temperature and relative humidity sensors; CR1, CR2 – sampling and focusing cryotraps; N<sub>2</sub>, He – nitrogen and helium cylinders; small clouds depict overflow outlets. The parameters which are underlined in red are recorded during measurements.







**Fig. 2.** The standard two-hour cycle of measurements. The signal observed at m/z 81.069 is shown as an example, and the color indicates what is measured at a given moment (see legend). The brackets in the plot area indicate GC sampling and ozone addition periods. Colored lines under the *x* axis depict the averaging/integration period for averaged/integrated data as used in Fig. 3 and 7: last 7 min of first reaction chamber air, last 4 min of purified air, last 9 min of plant chamber air, last 9 min of second plant chamber air, last 7 min of second reaction chamber air (ozone treatment).



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**Fig. 3.** Online measured mixing ratios in the plant chambers (diamonds) and in the reaction chamber without ozone addition (asterisks), experiment B. The respective background levels (purified air) are shown as continuous lines. The shaded area indicates the dark period.







**Fig. 4.** Example gas chromatograms of experiment A. For every profile running mean over 5 points is used. The green line and the blue line correspond to sampling the ozonated and non-ozonated reaction chamber, respectively. The black line is a background chromatogram. m/z 45.033 corresponds to acetaldehyde, m/z 87.081 to methyl buthenol (MBO), m/z 81.069 to monoterpenes and additional compounds, m/z 137.133 to monoterpenes only.





**Fig. 5.** Ozonolysis of  $\beta$ -pinene. The top panel shows the course of ozone and  $\beta$ -pinene (sum of m/z 81.069 and 137.133). The lower panels show oxidation products detected at m/z 31.018 (formaldehyde), 47.013 (formic acid), 121.102 and 139.112 (attributed to nopinone), 153.092 (C<sub>9</sub>H<sub>13</sub>O<sub>2</sub><sup>+</sup>), and 155.107 (C<sub>9</sub>H<sub>15</sub>O<sub>2</sub><sup>+</sup>). Ozone was added to the reaction chamber 85 min after the start of the measurements. Presented points are averaged mixing ratios of 11.5 min time periods, which corresponds to the residence time of the air in the reaction chamber.











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**Fig. 7.** Online measured mixing ratios of monoterpenes (MTs) and m/z 73.029 in the reaction chamber without ozone addition (asterisks) and during/after ozone addition (diamonds), experiment B. The shaded area indicates the dark period.



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