SSD

SCIENCE FOR A SUSTAINABLE DEVELOPMENT

Impact of **P**henology and **E**nvironmental **C**onditions on B**VOC** Emissions from Forest Ecosystems

IMPECVOC

J. DEWULF, É. JOÓ, H. VAN LANGENHOVE, O. POKORSKA, K. STEPPE,
R. LEMEUR, M. ŠIMPRAGA, H. VERBEECK, J. BLOEMEN,
M. DEMARCKE, C. AMELYNCK, N. SCHOON, J.-F. MÜLLER,
Q. LAFFINEUR, M. AUBINET,

ENERGY

TRANSPORT AND MOBILITY

AGRO-FOOD

HEALTH AND ENVIRONMENT

CLIMATE

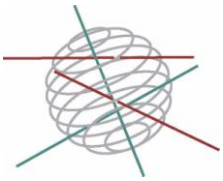
BIODIVERSITY

ATMOSPHERE AND TERRESTRIAL AND MARINE ECOSYSTEMS

TRANSVERSAL ACTIONS

.be

SCIENCE FOR A SUSTAINABLE DEVELOPMENT
(SSD)



Climate & Terrestrial ecosystems

FINAL REPORT

IMPACT OF PHENOLOGY AND ENVIRONMENTAL CONDITIONS ON BVOC EMISSIONS FROM FOREST ECOSYSTEMS

«IMPECVOC»

SD/TE/03

Promotors
Kathy Steppe / Raoul Lemeur - UGent
Jo Dewulf / Herman Van Langenhove - UGent
Crist Amelynck / Niels Schoon / Jean-François Müller - BISA
Marc Aubinet - FUSAGx

Authors
J. Dewulf, E. Joó, O. Pokorska, H. Van Langenhove, K. Steppe, R. Lemeur, M. Šimpraga, H. Verbeeck, J. Bloemen, M. Demarcke, C. Amelynck, N. Schoon, J.-F. Müller, Q. Laffineur, M. Aubinet, B. Heinesch

UNIVERSITEIT GENT

EnVOC Environmental Organic Chemistry and Technology Research Group

gembloux faculté universitaire des sciences agronomiques

UNIVERSITEIT GENT LABORATORIUM PLANTECOLOGIE

D/2012/1191/24
Published in 2012 by the Belgian Science Policy
Avenue Louise 231
Louizalaan 231
B-1050 Brussels
Belgium
Tel: +32 (0)2 238 34 11 – Fax: +32 (0)2 230 59 12
http://www.belspo.be

Contact person: Martine Vanderstraeten
+32 (0)2 238 36 10

Project Website: http://www.impecvoc.ugent.be/

J. Dewulf, E. Joó, O. Pokorska, H. Van Langenhove, K. Steppe, R. Lemeur, M. Šimpraga, H. Verbeeck, J. Bloemen, M. Demarcke, C. Amelynck, N. Schoon, J.-F. Müller, Q. Laffineur, M. Aubinet, B. Heinesch. ***"Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems IMPECVOC"***. Final Report. Brussels: Belgian Science Policy 2012 - 89 p. (Research Programme Science for a Sustainable Development).

Table of content

PROJECT TEAM

Partner 1 (Coordinator of phase 1):	**PE-UG**
Responsible:	Prof. dr. ir. Kathy Steppe/ Prof. Dr. Raoul Lemeur
Researchers:	Msc Maja Šimpraga, dr. ir. Hans Verbeeck
Student:	Jasper Bloemen
Institute:	Laboratory of Plant Ecology, Faculty of Bioscience Engineering, Ghent University (PE-UG)
Address:	Coupure links 653, 9000 Gent
Phone / fax:	+32 9 264 61 12 / +32 9 224 44 10
Partner 2 (Coordinator of phase 2):	**EnVOC-UG**
Responsible:	Prof. dr. ir. Jo Dewulf / Prof. dr. ir. Herman Van Langenhove
Researchers:	Éva Joó, Olga Pokorska
Students:	Lieselotte Schietse, Dora Neina
Institute:	Research Group Environmental Organic Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University (EnVOC –UG)
E-mail:	jo.dewulf@ugent.be
Partner 3:	**BISA**
Responsible:	dr. Crist Amelynck/ dr. Niels Schoon / dr. Jean-François Müller
Researchers:	Marie Demarcke
Institute:	Belgian Institute for Space Aeronomy (BISA)
Partner 4:	**FUSAGx - UBP**
Responsible:	Prof. dr. Marc Aubinet
Researchers:	Quentin Laffineur, dr. Bernard Heinesch
Institute:	Faculté Universitaire des Sciences Agronomiques de Gembloux, Unité de Physique des Biosystèmes (FUSAGx - UBP)

ACRONYMS AND ABBREVIATIONS

AA	Abies Alba
AF	Aelmoeseneie Forest
BELSPO	Belgian Federal Science Policy Office (Belgisch Federaal Wetenschapsbeleid)
BIRA	Belgisch Instituut voor Ruimte-Aëronomie (BIRA) / Belgian Institute for Space
(BISA or IASB)	Aeronomy (BISA)/ Institut d'Aéronomie Spatiale de Belgique (IASB) (Partner P3)
BVOC	Biogenic volatile organic compounds
CA	Campus
CCI	Chlorophyll Content Index
Co	Coordinator (Partner P1), i.e. Prof. dr. Raoul Lemeur/ Prof. Dr. Ir. K. Steppe and their team (PE-UG)
$[CO_2]$	Atmospheric CO_2 concentration
Chl	Chlorophyll
Cuv 1	Cuvette 1
Cuv 2	Cuvette 2
Cuv ref	Cuvette reference
D	Diameter
DAQ	Data acquisition unit
EC	Eddy-covariance
EnVOC-UG	Research Group Environmental Organic Chemistry and Technology, Ghent University (Partner P2)
EQ	Equitensiometer
FE	Fraxinus Excelsior
FNRS	Fonds National de Recherche Scientifique
FOV	Field of view
FS	Fagus Sylvatica
FUSAGx	Faculté Universitaire des Sciences Agronomiques de Gembloux (Partner P4)
FWO	Fonds voor Wetenschappelijk Onderzoek
G97	Isoprene emission algorithm (Guenter, 1997)
G06	MEGAN isoprene emission algorithm (Guenter et al., 2006)
G06a	Modified version of MEGAN isoprene emission algorithm
GC-MS	Gas chromatograph – mass spectrometer
GR	Growth Room
I	Irradiance
IMPECVOC	Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems
INBO	Instituut voor Natuur- en Bosonderzoek (Research Institute for Nature and Forest)
IR	Infrared radiation
IRGA	Infrared gas analyzer
IRTC	Infrared thermocouple
ISTD	Internal standard
IWT	Instituut voor de Aanmoediging van Innovatie door Wetenschap en Technologie in Vlaanderen
KMI	Koninklijk Meteorologisch Instituut van België (Royal Meteorological Institute of Belgium)
LA	Leaf area

LAI	Leaf area index
LD	Larix Decidua Mill.
LVDT	Linear variable displacement transducer)
MACR	metacrolein
MDS	Maximum daily shrinkage
MT	Monoterpenes
MVK	Methyl vinyl ketone
NDVI	Normalized difference vegetation index
OVOC	Oxygenated volatile organic compounds
Pn or A	Net photosynthesis or net CO_2 assimilation rate (µmol-CO_2 m^{-2} s^{-1})
P1	Partner 1, i.e. Prof. dr. Raoul Lemeur/Prof. Dr. Ir. K. Steppe and their team (PE-UG)
P2	Partner 2, i.e. Dr. Crist Amelynck and his team (BISA)
P3	Partner 3, i.e. Prof. dr. Jo Dewulf and his team (EnVOC – UG)
P4	Partner 4, i.e. Prof. dr. Marc Aubinet and his team (UBP)
PAR	Photosynthetically active radiation (µmol-photons m^{-2} s^{-1})
PE-UG	Laboratory of Plant Ecology, Ghent University (Partner P1)
PM	Pseudotsuga menziesii (Mirb) Franco
PN	Pinus Nigra
PPDF	Photosynthetic photon flux density
PTR-MS	Proton transfer reaction - mass spectrometry (spectrometer)
RH	Relative humidity
RRI	Relative retension time
Q	Mass flow
QR	Quercus Robur
SEF	Standard emission factor
SIM	Selective Ion Monitoring
SLA	Specific leaf area
SPDE	Solid phase dynamic extraction
SQT	Sesquiterpenes
SRI	Switchable reagent ion
SWC	Soil water content
TDP	Thermal dissipation probe
TIC	Total ion chromatogram
Tl	Leaf temperature
Tr	Transpiration rate
UA	University of Antwerp
UBP	Unit of Biosystem Physics (Unité de Physique des Biosystèmes) Faculté Universitaire des Sciences Agronomiques de Gembloux (Partner P4)
vDEC	virtual Disjunct eddy-covariance
VMM	Vlaamse Milieumaatschappij
VOC	Volatile organic compound
VPD	Vapor pressure deficit
VPD_{air}	Air vapour pressure deficit
WP	work package
m/e or m/z	mass to charge ratio
ncps	normalized counts per second
ng	nanogram
ppbv	parts per billion (by volume)
ppm	parts per million
ppmv	parts per million (by volume)
pptv	parts per trillion (by volume)

SUMMARY

A. Context

Forest ecosystems are known to be important sources of Biogenic Volatile Organic Compounds (BVOC). Due to their large emissions and their high reactivity with the main oxidants (OH, O_3, NO_3) in the atmosphere, these BVOCs play an important role in atmospheric chemistry. In order to be able to quantify net formation of oxidants and aerosols from BVOCs, the physicochemical oxidation and aerosol formation and/or growth have to be well understood. Of equal importance, however, is that BVOC emissions need to be well characterized and quantified. Few experimental data are available on the effect of temperature and radiation history on emissions. Measurements are needed to determine the precise dependence of emissions upon radiation and leaf temperature for tree species commonly found in Belgium. The advent of new on-line, rapid and sensitive technologies such as the Proton Transfer Reaction Mass Spectrometer (PTR-MS) has opened new and exciting developments in BVOC emission research. As such direct eddy-covariance BVOC flux measurements at the level of a forest stand became possible. PTR-MS is also very useful to perform long-term continuous BVOC emission measurements from branch enclosures (e.g. leaf cuvettes).

B. Objectives

The objectives of the IMPECVOC project are: (1) The collection of BVOC emission data at different levels of biological organisation (leaf emissions from young model trees in climate controlled growth chambers; emissions from horizontal leaf canopy layers observed on the measuring tower at the Aelmoeseneie experimental forest; and emission measurements above the large Vielsalm experimental forest); (2) The validation of new emission algorithms (adaptation of the MOHYCAN canopy model and the MEGAN model which allow spatial upscaling of BVOC emissions from leaf to tree and to stand level); (3) The correction of emission algorithms by inclusion of additional driving variables (e.g. water availability, atmospheric CO_2 concentration and effects of forest functioning (e.g. seasonal leaf area development, leaf age, sunlit and shaded leaves, …); and (4) The estimation of the BVOC emissions from Belgian forests based on the modified emission algorithms and Belgian forest inventories.

During phase 1 of the IMPECVOC-project simultaneous BVOC (PTR-MS and GC-MS), CO_2 and H_2O flux measurements have been carried out on a regular time scale during the branch enclosure experiments in the growth room and at the Aelmoeseneie experimental forest. In order to perform dynamic branch enclosure

flux measurements, prototype cuvettes were designed and constructed. In addition, during the first trimester of 2008, in between the experiments in the growth chamber and the field measurements in the Aelmoeseneie forest, laboratory measurements were performed in order to study the influence of instrumental and environmental parameters on the detection of sesquiterpenes with the PTR-MS instrument.

C. Conclusions

The results showed that beech (*Fagus sylvatica* L.) is a low isoprene emitter and a rather strong monoterpenoid emitter. A clear link was observed between temperature variation and monoterpenoid emissions, linked to net photosynthesis rates. The results revealed that the potted beech tree under well-watered conditions re-emitted a rather low fraction of the assimilated carbon back into the atmosphere as total monoterpenoids. This fraction increased exponentially from 0.01 to 0.10 % with a temperature rise from 17 °C to 27 °C in growth room conditions.
From the results of the drought experiment it was seen that monoterpenoid emissions were linked to tree physiology; more specific to leaf net photosynthesis rate, to stem diameter growth and to sap flux density. Moreover, interdependence between leaf and tree plant processes was observed. Imposed severe drought caused photosynthesis and monoterpenoid emissions to decrease. Upon photosynthesis inhibition, the emissions of monoterpenoids were inhibited most likely due to the photosynthetic origin of the monoterpenoids. Data of the canopy experiment in the Aelmoeseneie forest clearly showed that there was a difference between sunlit leaves and shade-adapted leaves. Diurnal BVOC emission patterns indicated that shade-adapted leaves for a sunny day show a stronger interaction between monoterpenoid emissions and net photosynthesis than for the sunlit leaves. This interaction was even stronger for a cloudy day. It can, hence, be stated that the physiological leaf status plays a major role when considering monoterpenoid emissions, photosynthesis and transpiration rates. The importance of the physiological status of leaves should therefore be emphasized more in the future.
Based on the experimental data, existing emission algorithms could be tested and improved. This work is still ongoing. The observed emissions are more closely approximated using isoprene emission algorithms than by using a light-independent monoterpene emission algorithm developed for coniferous trees. PTR-MS measurements in the growth room under controlled conditions and in the Aelmoeseneie forest under real outdoor conditions already revealed the effect of light history on monoterpenoid emissions by *Fagus sylvatica* L., which is not correctly incorporated in commonly used emission algorithms. Modifications of these algorithms have been proposed for an accurate description of this effect.
At the end of phase 1, the operational infrastructure at the Vielsalm forest site was established and the stand-scale experiment has been the major focus of phase 2 of the project. This infrastructure includes a meteorological tower fully equipped with adequate sensors, and an equipped shelter. The existing set-up had to be strongly

updated for BVOC measurements. Joint efforts of all four partners led to the collection of the large dataset from the site of Vielsalm. Partner 1 focused on spatial and seasonal variation of leaf area index (LAI) in the footprint of the flux measurement tower. Partner 3 and 4 collected BVOC and (micro)meteorological data respectively, from the top of the 52 m high tower while Partner 2 sampled air on a monthly basis for GC-MS analysis. Partner 4 mainly investigated the isoprene, monoterpenes and the methanol fluxes. Since this measurement campaign has finished recently (November 2010) data analysis and interpretation is still ongoing.

D. Contribution of the project in a context of scientific support to a sustainable development policy

Policy makers bring the framework to have proper environmental living conditions for the people. In this sense they rely on scientific data to establish a proper policy for a healthy atmosphere. To that extent, European countries like Belgium are forced to make inventories about compounds emitted by mankind and nature that influence the atmospheric quality. It turns out that for the category of volatile organic compounds with quite different impacts such as contribution to tropospheric ozone formation, global warming and human toxicity, forests are quite important contributors. In this sense, emission inventories BVOCs are essential in proper decision making. The emission inventory of BVOCs currently relies on models that are based on measurements and models from the early 1990s.
Our project results provide measurements and models that are a first step towards a better estimation of BVOC emissions. First, we learn that there are more factors than tree species, light and temperature that determine the emission of BVOCs. For example, seasonality, the physiological status of the leaves and infection influence the emissions. Second, we learn that a number of compounds are emitted which do not get proper attention in emission inventories and that may be of interest in further atmospheric chemistry, in particular in ozone formation and particulate matter development. In a further stage, these findings could be the base of a refined BVOC emission estimation providing a sound basis for proper policy with respect to atmospheric quality.

1. Introduction

Forest ecosystems are known to be important sources of Biogenic Volatile Organic Compounds (BVOC). Due to their large emissions and their high reactivity with the main oxidants (OH, O_3, NO_3) in the atmosphere, these BVOCs play an important role in atmospheric chemistry. In the presence of nitrogen oxides, atmospheric oxidation of BVOCs may for instance result in net oxidant formation that has an important impact on air quality and tropospheric chemistry. Less volatile oxidation products can lead to the formation and/or growth of aerosol particles and, as such, have an important impact on health, visibility and climate (through scattering and absorption of solar radiation and cloud formation). In order to be able to quantify net formation of oxidants and aerosols from BVOCs, the physicochemical oxidation and aerosol formation and/or growth have to be well understood. Of equal importance, however, is that BVOC emissions need to be well characterized and quantified as well.

It is well-established that photosynthetic photon flux density (PPFD) and leaf temperature (Tl) strongly influence BVOC emissions from plant leaves. Few experimental data are available on the effect of temperature and PPFD history on emissions. Measurements are needed to determine the precise dependence of emissions upon PPFD and Tl for tree species commonly found in Belgium. Far less is known about the effects of other environmental conditions (e.g. relative humidity of the air, soil water availability, atmospheric CO_2 concentration); and of tree physiology, forest functioning and forest phenology. In order to reduce uncertainties on BVOC emissions from forest ecosystems these effects should be incorporated in BVOC emission algorithms as well. If not, BVOC emission estimates from the simple PPFD and Tl based algorithms will be less precise and include large systematic errors.

The advent of new on-line, rapid and sensitive technologies, such as Proton Transfer Reaction Mass Spectrometry (PTR-MS), has opened new and exciting developments in BVOC emission research. As such direct eddy-covariance BVOC flux measurements at the level of a forest stand became possible. PTR-MS is also very useful to perform long-term continuous BVOC emission measurements from branch enclosures (e.g. leaf cuvettes).

At present, eddy-covariance BVOC flux measurements based on PTR-MS have been carried out by only a limited number of research groups worldwide (e.g. Rinne et al., 2001; Karl et al., 2002; Grabmer et al., 2004; Spirig et al., 2005) but the number of measurement locations in Europe is still very small. Also, measurements were only made during a small fraction of the growing season.

In contrast to the previously mentioned studies, the present research program will also focus on the temporal dynamics of BVOC emissions during a complete growing season, during which forests functioning and forest phenology will be followed at the same time.

Objectives

The objectives of the IMPECVOC project are:
(1) The collection of BVOC emission data at different levels of biological organisation (leaf emissions from young model trees in climate controlled growth chambers; emissions from horizontal leaf canopy layers observed on the measuring tower at the Aelmoeseneie experimental forest; and emission measurements above the large Vielsalm experimental forest);
(2) The validation of new emission algorithms (adaptation of the MOHYCAN canopy model and the MEGAN model which allow spatial upscaling of BVOC emissions from leaf to tree and to stand level);
(3) The correction of emission algorithms by inclusion of additional driving variables (e.g. water availability, atmospheric CO_2 concentration, and effects of forest functioning (e.g. seasonal leaf area development, leaf age, sunlit and shaded leaves,…); and
(4) The estimation of the BVOC emissions from Belgian forests based on the modified emission algorithms and Belgian forest inventories.

The expected outcomes are:
(1) An improved insight in the fundamental plant processes which govern BVOC emissions;
(2) The availability of validated emission algorithms with better precision as more abiotic and biotic driving variables are taken into account;
(3) The establishment of practical calculation procedures for upscaling and estimation of BVOC emissions at stand level; and
(4) The elaboration of regional and national BVOC emission inventories.

2. Methodology and results

For an extensive description of the materials and methods used in the IMPECVOC project we refer to the previous reports of this project. Nevertheless, several crucial methodological issues are discussed in the results section below.

The results are described below according to each workpackage as described in the IMPECVOC project proposal.

WP1 Comparison GC-MS and PTR-MS

1.1 Experimental setup for coupling PTR-MS and GC-MS

For GC-MS analysis of BVOCs pre-concentrated on adsorbent sampling tubes were used (Figure **1**). The tubes were selected by considering three major points as: (i) complete adsorption of VOCs in a qualitative and quantitative way should be obtained; (ii) artefacts which are formed on the tube, especially when ozone is present during sampling, should be avoided; and (iii) interference with water during the analysis should be eliminated. Therefore, the decision – based on literature (Helmig, 2006; Dominguez-Taylor, 2007; Ormeno, 2007; Tiiva, 2007; Liakakou, 2007) – was taken to use multiple adsorbent tubes containing Tenax TA (35 m²/g, MARKES) and Carbotrap (100 m^2/g, 20-40 mesh, MARKES) with a ratio of 50:50 packed in glass tubes (O.D. 0.25-inch, length 3.5 inch). Analyses were performed with an on-line coupled Unity thermal desorber and air server (MARKES International, Pontyclum, UK) and a GC Trace 2000 gas chromatograph (ThermoFinnigan, Milan, Italy) connected to a MS Trace DSQ WE-250 mass spectrometer (ThermoFinnigan, Austin, TX, USA). After desorption of the concentrated compounds, they were separated on a DB-1 (30 m x 0.25 mm x 1 µm) column placed inside the GC and then ionized and detected in the MS. In some cases the Ultra Autosampler (QUI-0006 3.1) was used instead of the mentioned thermal desorber. The whole system is controlled from a personal computer (Compaq PC-EVO-310) with Unity 1.2.0 (MARKES International) and XCalibur 1.3 (ThermoFinnigan, Austin, TX, USA) software installed.

Figure 1: From left to right: (a) adsorbent sampling tubes, (b) GC-MS and (c) scheme of GC-MS work principle.

In order to perform accurate BVOC concentration measurements with the PTR-MS instrument (Figure 2a) an additional experimental set-up for determining the instrumental background and for calibrating the PTR-MS for the BVOCs of interest has been designed and constructed at BISA (Partner P3). This set-up mainly consists of a catalytic converter for generating a zero-VOC air flow, a calibration gas mixture containing trace amounts of methanol, ethanol, acetone, isoprene and monoterpenes (sabinene and α-pinene) diluted in N_2 (Apel-Riemer Inc., Denver, CO), a set of mass flow controllers and three-way solenoid valves, a diaphragm pump for generating a gas flow, and power supplies for the flow controllers and solenoid valves. To enable alternate sampling from multiple cuvettes in growth chamber experiments, as well as in the canopy experiment, a gas multiplexer (Figure 2c) has also been constructed. All gas lines and the inner surfaces of the solenoid valves (in the calibration set-up as well as in the multiplexer) are made of Teflon and PFA (polyfluoro alkoxy Teflon) to avoid losses of BVOCs. The output direction of the three-way valves and the setpoints of the flow controllers are set through a HP DAQ (Figure 2b), which also serves to log the valve positions and the flow controller output values continuously. The DAQ in turn is controlled by a LabVIEW based software program (developed at BISA); and both this program and the PTR-MS software program can be run from any location by using remote PC control. PTR-MS calibration and background measurements, as well as alternate BVOC emission measurements from different cuvettes can be performed in an automatic mode by using scripts (set of command lines). The entire set-up is constructed in such a way that it can easily be transported between the growth chambers and the two forest sites. Close to the location where the PTR-MS capillary inlet line is connected to this set-up, an additional inlet (which can be shut off with a PFA stop valve) is foreseen for Partner P2 (ENVOC) in order to use the same calibration standard as BISA and to perform simultaneous measurements. The above described additional experimental set-up works successfully.

Figure 2: From left to right: (a) PTR-MS set-up, (b) DAQ and (c) multiplexer.

1.2 Calibration PTR-MS and GC-MS

The methodology for calibrating GCMS and PTRMS for the target compounds has been described in detail in the final report of phase I of the IMPECVOC project (§ 1.1 and 1.2).

Calibration of the PTR-MS signals at m/z=33 (methanol), m/z=45 (acetaldehyde), m/z=59 (acetone), m/z=69 (isoprene), m/z=81 and 137 (sum of monoterpenes) has been performed every 2 to 4 days during the measurement campaign at the Vielsalm forest (26/06-17/11/2009 and 26/03-18/11/2010). The smooth variation of the respective calibration factors during the 2009 campaign is shown in Figure 3 as illustration.

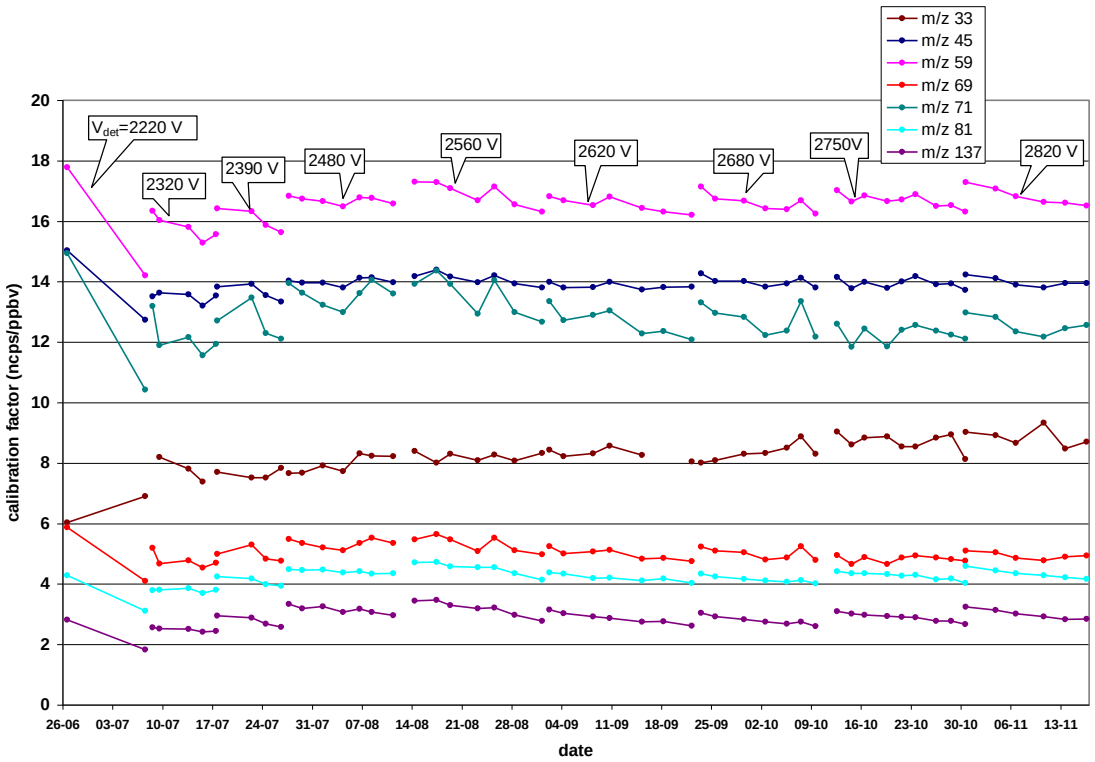


Figure 3: Variation of the calibration factors of methanol (m/z=33), acetaldehyde (m/z=45), acetone (m/z=59), isoprene (m/z=69), MVK+MACR (m/z=71) and the sum of the monoterpenes (m/z=81 and 137) during the 2009 measurement campaign at the Vielsalm forest.

However, until mid July 2010 the calibration mixture of BISA (P3), which was used for these calibrations, did not contain methyl vinyl keton (MVK) and methacrolein (MACR), which are needed for the calibration of the PTR-MS signal at m/z=71. On 16/09/2009 PTR-MS calibrations were carried out with the gas mixture of BISA and with a second mixture from the group "Plant and Vegetation Ecology" of the University of Antwerp. The latter mixture contains the same compounds as the one of BISA plus some additional compounds, such as MVK and MACR. The calibrations on 16/09/2009 therefore allowed us:

- firstly to determine the calibration factor for the sum of the compounds MVK and MACR for one single day. Since the PTR-MS signal of isoprene at m/z=69 is very close to the one of (MVK+MACR) at m/z=71, it is not expected that the ratio of the respective calibration factors will change with time due to the aging of the detector. From this constant ratio, determined with the calibration mixture of the University of Antwerp, and the calibration factor of isoprene, which was measured regularly, the calibration factor for

(MVK+MACR) could be derived for the whole 2009 measurement campaign, as is shown in Figure 1.

- secondly to compare the calibration factors obtained with both mixtures. The difference between the calibration factors was better than 5%, which is in agreement with the accuracy of the mixing ratio of the different compounds in these mixtures given by the manufacturer.

From July 19th 2010 on a new calibration mixture was used by P3, which additionally contained MVK and MACR. For the period of the 2010 measurement campaign before July 19th the calibration factor for the PTR-MS signal at m/z 71 was derived from the ratio of the calibration factors of isoprene and (MVK+MACR) determined on July 19th 2010.

In 2010 two compounds, formic and acetic acid, were added to the list of BVOCs for routine eddy-covariance measurements. The calibration mixture does however not contain these two compounds. Since acetaldehyde, formic acid, acetone and acetic acid mainly have one product ion, i.e. the corresponding protonated molecule, at m/z 45, 47, 59 and 61 respectively, and since the m/z values of the product ions of acetaldehyde and formic acid are very close (idem for acetone and acetic acid), the calibration factors of acetaldehyde and acetone are good estimates of the calibration factors of formic and acetic acid respectively.

In between the 2009 and 2010 measurement campaign the dependence of the PTR-MS calibration factors of the different compounds on the water vapour concentration in the drift tube of the PTR-MS was investigated at BISA in detail. A possible dependence of the calibration factors on this water concentration has to be taken into account during the data analysis of the eddy-covariance measurements, since varying humidity of the air sampled will be reflected in the water concentration in the drift tube and therefore influence the ion chemistry taking place in the reaction zone of the PTR-MS. The calibration factors of methanol, acetone, acetaldehyde and the sum of the monoterpenes only showed a very slight dependence on the water concentration in the drift tube (variation of the calibration factor less than or equal to the error on the calibration factors). However, the calibration factors of isoprene and of the sum of MVK and MACR show a non-negligible dependence, as is illustrated in Figure 4. The normalized PTR-MS signal at m/z 39 (third isotope of the precursor ion $H_3O^+.H_2O$) mentioned on the x-axis of this figure is a relative measure of the water concentration in the drift tube of the PTR-MS. For the 2010 measurement campaign the dependence of the calibration factors of isoprene and of the sum of MVK and MACR on the water concentration has been determined on a monthly basis.

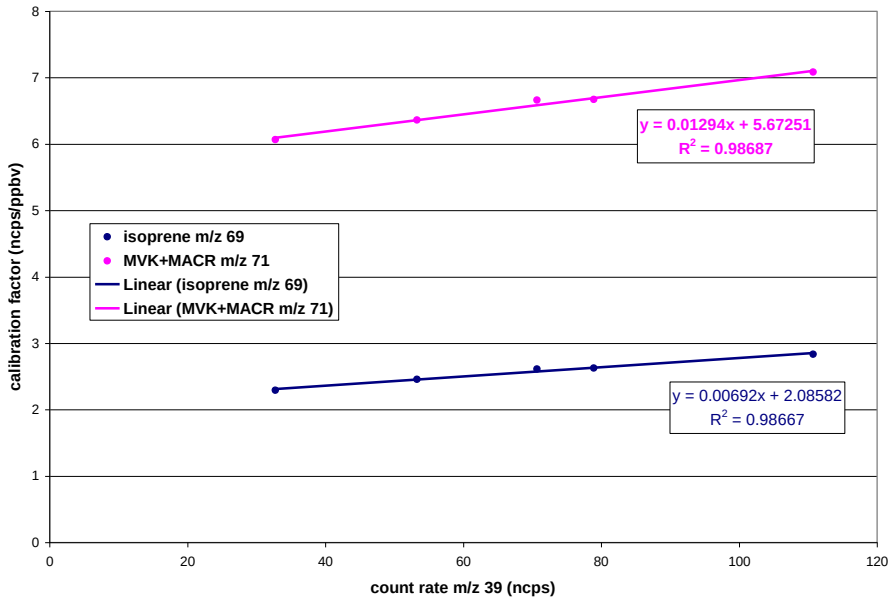


Figure 4: dependence of the calibration factors of isoprene m/z 69 and (MVK+MACR) m/z 71 on the water concentration in the drift tube.

In January 2010 the PTR-MS instrument was upgraded to a proton-transfer-reaction mass-spectrometer with switchable reagent ion capability (PTR+SRI-MS), allowing to switch relatively fast between H_3O^+, NO^+ and O_2^+ precursor ions. The use of different kinds of precursor ions allows the quantification of some isobaric compounds, which normally cannot be distinguished from each other by using H_3O^+ precursor ions only. For example, MVK and MACR give both rise to a PTR-MS signal at m/z 71 when H_3O^+ precursor ions are used. Therefore only the sum of the concentrations of MVK and MACR can be derived in the H_3O^+ mode. When NO^+ precursor ions are used two fingerprint PTR-MS signals at m/z 69 and m/z 100 are observed. If the m/z 69 signal can be linked with MACR and the m/z 100 signal with MVK, MVK and MACR can be quantified separately. This was verified on July 21st 2010: ambient concentrations of MVK and MACR quantified separately by using NO^+ precursor ions agreed well with the sum of the concentrations of MVK and MACR determined by using H_3O^+ precursor ions. However, due to the fact that some measurement time was lost in July (necessary maintenance of the PTR-MS) and August 2010 (instrument breakdown due to malfunctioning of a heating module) and taking into account the rather bad weather conditions in the month of August, it was decided for the remaining part of the 2010 measurement campaign not to exploit this new feature of the PTR-MS and to completely focus on the major task of eddy-covariance measurements with H_3O^+ precursor ions.

1.3 Intercomparison growth chamber

PTR-MS and GC-MS data were intercompared and validated in the growth chamber experiment. The analysis of this intercomparison is described under 1.5.

1.4 Intercomparison forest sites

PTR-MS and GC-MS data were intercompared and validated in the forest experiment. The analysis of this intercomparison is also described under 1.5.

1.5 Data analysis

Intercomparison of PTR-MS and GC-MS branch enclosure measurements

Simultaneous PTR-MS and GC-MS measurements were compared in a quantitative way for the emitted BVOCs. The methodology applied in this intercomparison has been previously described in detail (see Final Report of Phase 1).
By being a very fast and sensitive on-line analyzer, a PTR-MS occupies an unique position in VOC research. However, quantification of individual VOCs by PTR-MS can be hampered by the absence of a unique estimator ion for the compound of interest due to overlapping m/z ratios of ion signals originating from several VOCs that are present in the air sample.
Monoterpenes have been measured by PTR-MS on many occasions by several research groups and the PTR-MS ion signal at m/z 137 ($C_{10}H_{17}^+$) has always been considered as a good estimator ion for the sum of MTs, as was sometimes verified by complementary GC measurements. Therefore, the ion signal at m/z 137 was selected for quantification of MTs in the PTR-MS. In the course of the experiments the relative contribution of linalool compared to that of MTs was found to be up to 84% (Figure 5).

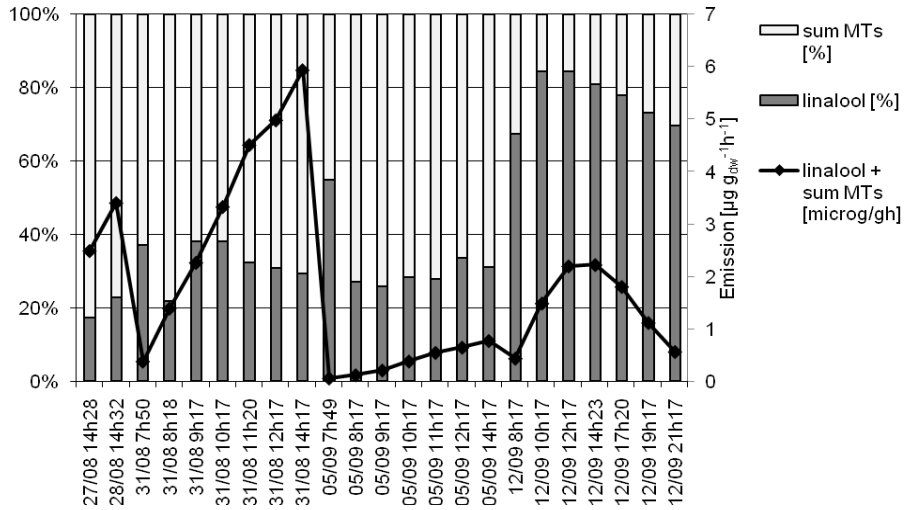


Figure 5: Relative contribution of linalool to the sum of linalool and monoterpenes from *Fagus sylvatica* L. Results are based on GC-MS measurements. Also shown are absolute linalool + monoterpene emission rates in µg $g_{dw}^{-1}h^{-1}$.

Since linalool has also a PTR-MS signature at m/z 137, quantification of MT emission rates by PTR-MS was disturbed. In Figure 6 the measured MT emission rates based on GC-MS are plotted against those obtained from the PTR-MS signal at m/z 137. Linear regression resulted in a slope of 0.67 (R^2=0.953) and the PTR-MS MT emission rates were roughly twice as high as the GC-MS ones when the highest linalool contributions were observed.

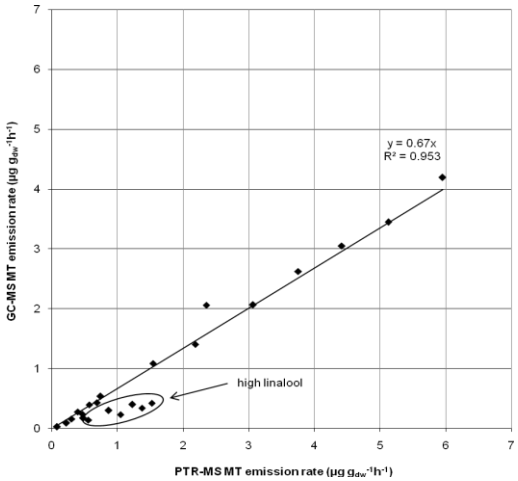


Figure 6: Measured GC-MS monoterpene emission rates versus those obtained by PTR-MS when assuming that no other compounds than monoterpenes contribute to the PTR-MS ion signal at *m/z* 137 (see text for more explanations). The largest deviations from the linear relationship (encircled data points) correspond to the highest contributions of linalool.

Comparison of GC-MS and PTR-MS data allowed an estimation of the ratio of the PTR-MS sensitivity for linalool to the one for MTs at m/z 137. This ratio of sensitivities, combined with the information of the relative contribution of linalool to the sum of linalool and MTs obtained by GC-MS, resulted in accurate derivation of the sum of emission rates of linalool and MTs by PTR-MS (Figure 7). The results indicate that fast and on-line PTR-MS measurements of BVOCs are best accompanied by off-line GC measurements to detect possible interferences or to use the additional information for properly quantifying the sum of emission rates of several compounds. More detailed information can be found in the article of Joó et al. “Quantification of interferences in PTR-MS measurements of monoterpene emissions from Fagus sylvatica L. using simultaneous TD-GC-MS measurements” (International Journal of Mass Spectrometry 291, 2010).

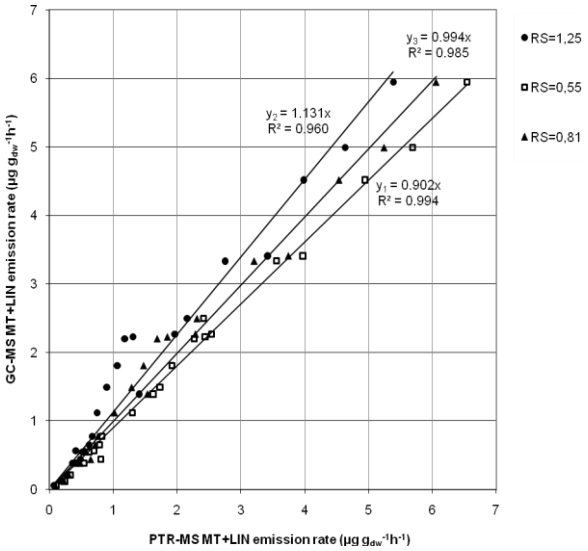


Figure 7 Comparison of GC-MS and PTR-MS emission rates of the sum of monoterpenes (MT) and linalool when taking into account a weighted PTR-MS sensitivity factor. RS is the ratio of the PTR-MS sensitivities of linalool and MTs based on the ion signal at *m/z* 137 ($S_{LIN,137}/S_{MT,137}$).

Comparison of simultaneous GC-MS and PTR-MS concentration measurements from the top of the eddy-covariance tower in Vielsalm

In the summer of 2009 BVOC flux measurements could be started with the on-line PTR-MS. Additionally, samples were taken for GC-MS analysis on a montly basis to determine the identity of the monitored BVOCs. Results of 2009 showed that isoprene, α-pinene, limonene and sabinene were detected in the samples taken for GC-MS analysis. These compounds are the typical contributors of *Fagus sylvatica* L. and *Pseudotsuga menziesii* tree species, which can be found in the mixed forest of Vielsalm. The average relative contributions of the individual terpenes were 34% isoprene, 27% α-pinene, 16% sabinene and 28% limonene (n=3) in 2009. In addition, camphene, β-pinene, α-terpinene and terpinolene were detected in 2010. Since limonene and isoprene show rather high contribution compared to previous investigations on *Fagus sylvatica* L. and *Pseudotsuga menziesii*, these compounds are expected to be the main emitted volatiles from *Picea abies* L. as a major tree species of the forest.

Preliminary intercomparison between GC-MS and PTR-MS showed good agreement for the measurement of monoterpenes. Linear regression between monoterpene mixing ratios obtained with PTR-MS at the typical estimator ion signals at m/z 81 and m/z 137 and mixing ratios obtained with GC-MS resulted in slopes close to 1 (Figure 8). The PTR-MS signal of m/z at 69, used to monitor isoprene emissions, was in less agreement with the GC-MS measurements, which raises questions for further investigations. Laboratory intercomparison experiments are foreseen to test if particular compound(s) might have been interfering with the m/z at 81 signal, or loss of isoprene might have occured during the GC-MS sampling/analysis.

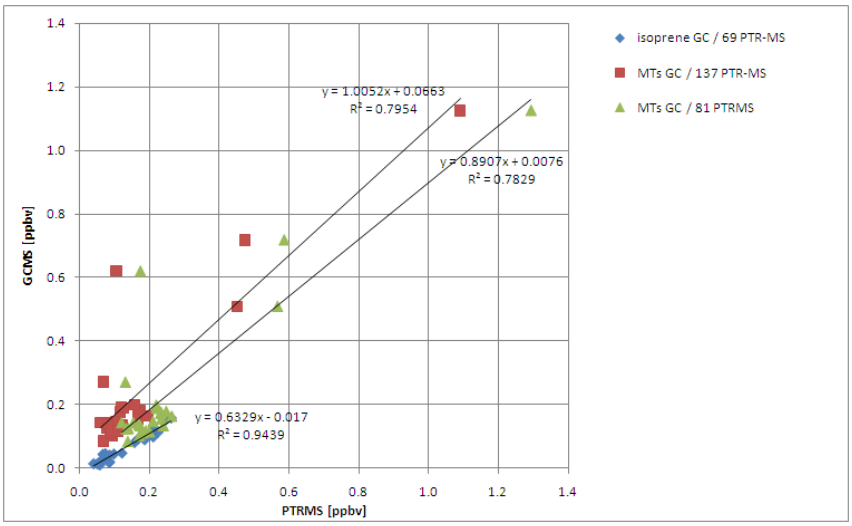


Figure 8: Intercomparison between GC-MS and PTR-MS for the measurement of monoterpenes (MT) and isoprene at the forest site of Vielsalm.

WP2 Growth chamber experiment

Growth chamber experiments were conducted according to the WP description in spite of some technical problems (e.g. PTR-MS detector and computer failures, IRGA BINOS instrument malfunctioning, lack of instrumentation in the beginning of the project…). The below summarized timing was followed once the growth rooms were operational and leaf cuvettes and analysis equipment were installed. This pre-preparation phase of the first year caused some delay in the start-up of the emission measurements. Nevertheless, the 2007-2010 campaigns were successful as very interesting relationships between BVOC emission from leaves of young trees and the driving variables and/or processes were obtained (leaf temperature variations, light response curves, net photosynthesis and transpiration (Tr) rates (*cfr.* Annual Scientific Report 2006/2007-2009).

Plant material and tree infestations (2007-2010)

In total seven tree species were examined: *Fagus sylvatica* L. (FS), *Quercus robur* L. (QR), *Fraxinus excelsior* L. (FE), *Pseudotsuga menziesii* (Mirb) Franco (PM), *Pinus nigra* L. (PN), *Abies alba* Mill. (AA) and *Larix decidua* Mill. (LD). Their specifications are indicated in the Table 1 below.

Table 1: Tree characteristics in controlled and natural conditions (2007-2010). Growth room (GR) and campus experiment (CA).

Exp. year	# trees	Tree sp.	Sam. Place	Size (cm)	Age (years)	Pot size (l)
2007	12	FS	GR	100-125	3	30
2008	12	FS	GR	125-150	4	40
2009	6	PM	GR	100-125	3	40
	3x used form 2008	FS	CA	125-150	5	40
	6	FS	CA	125-150	3	40
	6	QR	CA	150-200	3	40
	3	FE	GR	100-125	2	30
	3	FE	CA	200-250	3	40
	3	QR died	CA	100-125	2	30
2010	6	PN	CA+GR	125-150	5	40
	6	PM	CA	150-175	4	40
	6	PA	CA	150-175	3	40
	4	PT	CA	125-150	2	30
	4	LD	CA	125-150	4	40
	3	AA	CA	Vielsalm	Digged out	40
	3	AA	CA	Vielsalm	Digged out	40

During the 3.5 year period (2007-2010) in total 19 tree infestations were identified, insect as well as fungi, and are summarized in Table 2. A detailed infestation data base is available (P1).

Table 2: Identified infestations in controlled and natural conditions (2007-2010). Growth room (GR), campus experiment (CA), Aelmoeseneie forest (AF).

Tree species	Year	Sam. Place		Indentified insect/fungi
FS	2007	GR	1	*Phyllaphis fagi*
FS	2007	GR	2	*Nectria galligena*
FS	2008	GR	3	*Tetranychus urticae*
FS	2008	GR		*Phyllaphis fagi*
FS	2008	AF		*Phyllaphis fagi*
FS	2008	AF	4	unidentified caterpillar
PM	2009	GR	5	*Rhabdcline pseudotsugae*
PM	2009	CA	6	*Gilletteella cooleyi*
PM	2009	CA	7	*Phytophtora spp.*
FE	2009	CA	8	*Psyllopsis fraxini*
FE	2009	CA	9	unidentified species of family *Cecidomyiidae*
FE	2009	CA	10	*Phyllactinia fraxini* (powdery mildew)
FE	2009	CA	11	unidentified species of order Heteroptera
QR	2009	CA	12	*Tuberculoides annulatus*
QR	2009	CA	13	*Microsphaera alphitoides* (powdery mildew)
PN	2009	GR	14	*Rhyacionia buoliana*
PN	2009	CA	15	*Neodiprion lecontei*
PN	2009	CA	16	*Hylobius radicis*
PN	2009	CA	17	*Eulachnus rileyi*
AA	2010	CA	18	unidentified damage
LD	2010	CA		no damage
FS	2010	AF	19	*Mikiola fagi*

2.1 Tree cuvette

Design of an optimal branch cuvette for measurement of BVOC, CO_2 and H_2O vapour exchange from leaves

In order to perform dynamic branch enclosure BVOC, CO_2 and H_2O flux measurements, prototype cuvettes were designed and constructed (deliverable) in the mechanical workshop of BISA. In order to minimize losses of BVOCs to the walls, all cuvette parts that are in contact with the BVOCs are made of PFA or Teflon. The cuvettes consist of a transparent plexi glass base plate and three

support rings. Two rings are held together by aluminium bars and serve as support structure of a cylindrical 50 µ thick PFA foil with a transparency to PAR of 95 %. The base plate is also covered with PFA foil and contains an inlet and outlet opening in PFA and Teflon, a Teflon ventilator to homogenize the BVOC-enriched air inside the cuvette, and a Teflon structure for passing electrical wires (for the fan, thermistor, leaf temperature sensor, …) without creating air leaks. One of the rings of the cylindrical support structure is clamped to the base plate. Opposite to the base plate the branch enters the cylindrical enclosure and the cuvette is closed by means of a second cylindrical PFA envelope. On one end, the envelope is fixed to the support structure with a third aluminium ring and associated clamps. On the other end, it is wrapped and tightened around a branch of a tree. VOC-free air is pumped in the cuvette where it is enriched with BVOCs emitted by the leaves of the enclosed branch. Part of the BVOC-enriched air leaving the cuvettes is pumped towards the analytical instrumentation through PFA tubing. The rest is sent into the growth chamber. Three of these cuvettes have been manufactured and used in the course of the reporting period (Figure 9).

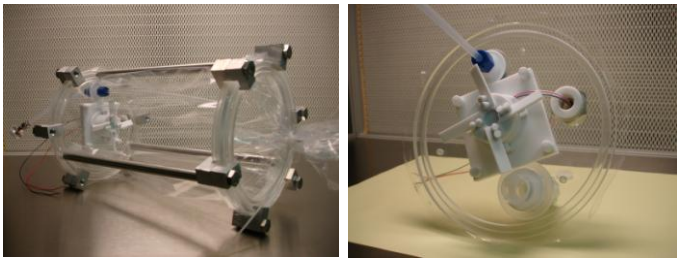


Figure 9: Prototype cuvette for inclusion of tree branches (left) and base plate with input and output connections (right).

To minimize BVOC losses only components in PFA or Teflon were used for the construction of the cuvettes and of the multiplexer. Possible BVOC losses (losses in the cuvette or in the PFA tubing in between the cuvette and the multiplexer or in the multiplexer itself, …) were characterized by introducing into the cuvettes a mixture with known concentration of monoterpenes, acetone and isoprene in VOC free air and by measuring the concentration of these compounds at different locations in between the cuvette and the PTR-MS (just after the cuvette, just in front of the multiplexer, after the multiplexer). It was found that the loss of BVOCs in the complete system is negligible (less than 2%).

Design of an inlet system of purified air into the cuvettes

To perform measurements of BVOC emissions with high accuracy purified air input lines for the cuvettes were necessary. Therefore, specific precautions had to be taken: (1) the removal of ozone present in ambient air; (2) the elimination of background VOCs; and (3) the adsorption of dust particles. As a solution, air was continuously taken from outside through an inlet line with a flow rate of 13.5 l/min

using a special membrane pump (MVP 055-3 diaphragm vacuum pump, PFEIFFER VACUUM, Aachen, Germany). To compensate for [CO_2] fluctuation in the inlet air flow, a 70 l buffer vessel was installed. A dust filter was added as well as MnO_2 as ozone scrubber. Two active coal filters were included for this purpose (DESOTEC N.V.-S.A.) and were placed in series, loaded by AIRPEL 10 and ORGANOSORB 10-CO in ascending order of specific area. Ensuring the absence of carry-over of carbon powder, a second dust filter was put before the flow splitting. Flow meters (5860S BROOKS Instruments) with valves were installed in each input line going to the cuvettes. All parts of this inlet line were connected by inert ¼ inch Teflon tubing. To ensure the quality of measurements and the data collected, ozone levels were checked monthly from the inlet air of cuvettes by a Z ECC Ozonesonde. This sensor is routinely used by the Royal Meteorological Institute of Belgium for atmospheric ozone measurements. Quantitative analysis is based on electrochemical reactions between ozone and potassium-iodide. It was found to be < 2 ppbv at all times.

2.2 Growth chamber measurements at optimal conditions

For the measurement of net photosynthesis (Pn) partner P1 used a CO_2 infra-red gas analyzer (IRGA). The same principle was used for measuring exchanges of water vapour in the cuvette due to transpiration. Photosynthesis is measured as a decrease in CO_2 concentration inside the cuvette when light is provided to the leaves. Respiration, on the other hand, is measured as an increase in CO_2 concentration that occurs when the cuvette is kept in darkness. In total during the project four different IRGAs were used: IRGA BINOS 100 4P, IRGA ADC 2250, IRGA LI-7000 and portable IRGA LI-6400. All IRGAs are explained in detail in previous project reports.
The aim was to study BVOC emissions (P3), CO_2 and water vapour exchange (P1) in different conditions. These measurements were done simultaneously during all experimental periods (Table 3). A level of 21°C was chosen as an optimal reference air temperature and PPFD was changed in a stepwise pattern. Prior to the growth chamber experiments, the trees were grown under a constant regime until new shoots were fully developed and mature. The same approach was used for the experiments at varying conditions (see section WP2.3)

Table 3: Long term experiment scheme in controlled and natural conditions (2007-2010). Abbreviations stand for: *Fagus sylvatica* L. (FS), *Quercus robur* L. (QR), *Fraxinus excelsior* L. (FE), *Pseudotsuga menziesii* (Mirb) Franco (PM), *Pinus nigra* L. (PN), *Abies alba* Mill. (AA), *Larix decidua* Mill. (LD), Aelmoeseneie forest (AF),Vielsalm (VL), cuvette (cuv), while experimental period (exp p).

	Experiment period 1	Experiment period 2	Experiment period 3	Experiment period 4	Experiment period 5
	(07 exp p1)	(07 exp p2)	(07 exp p3)	(07 exp p4)	
Species	*GR FS* 1, cuv1	*GR FS* 2, cuv1	*GR FS* 2, cuv1, cuv2	*GR FS* 2, cuv1, cuv2	*GR FS* 2, cuv1, cuv2
Experiment	test	temperature variation	temperature variation	CO2 experiment	senescence experiment
Dates	13/07/07 – 23/08/07	24/08 – 19/09/07	20/09/07 – 08/10/07	09/10/07 – 26/10/07	21/10/07 – 20/12/07
	(08 exp p1)	(08 exp p2)	(08 exp p3)	(08 exp p4)	
Species	*GR FS*	*AF FS*	*GR FS*	*AF FS*	
Experiment	seasonality	C1	drought stress	C2	data analysis
Dates	01/03/08-end	26/05/08-26/06/08	04/07/08-26/07/08	08/08/08-15/10/08	
	(09 exp p1)	(09 exp p2)	(09 exp p3)	(09 exp p4)	
Species	*GR PM*	CA QR, FE, FS (PM)	CA QR, FE, FS (PM)	*GR FS*	
Experiment	temperature variation	DECIDIOUS	DECIDIOUS	drought stress	data analysis
Dates	09/04/09-26/05/09			21/09/09-22/10/09	
	(10 exp p1)	(10 exp p2)	(10 exp p3)	(10 exp p4)	
Species	*GR PN* VL	CA AA, LD, PN (PM)	CA AA, LD, PN (PM)	CA AA, LD, PN (PM)	
Experiment	temperature variation	CONIFEROUS	CONIFEROUS	CONIFEROUS	data analysis
Dates	16/04/10-09/07/10	*VL*	*VL*	VL	
Experiment	light variation	*GR*	*GR*		data analysis
Dates	01/09/10-17/10/10	FS, cuv1, cuv2	FS, cuv1, cuv2		

Partner P2 joined to the continuous measurements at the beginning and at the end of the experimental period, and also for measurements at different temperatures. Samples were taken 15 min after PAR changes, which is the time necessary to reach constant IRGA and BVOC signal (checked by Partner P3). From the ozone measurements it was found that the constructed system is suitable for BVOC analysis, since O_3 presence was below 2 ppbv. BVOCs were successfully detected as it is shown in Figure 10.

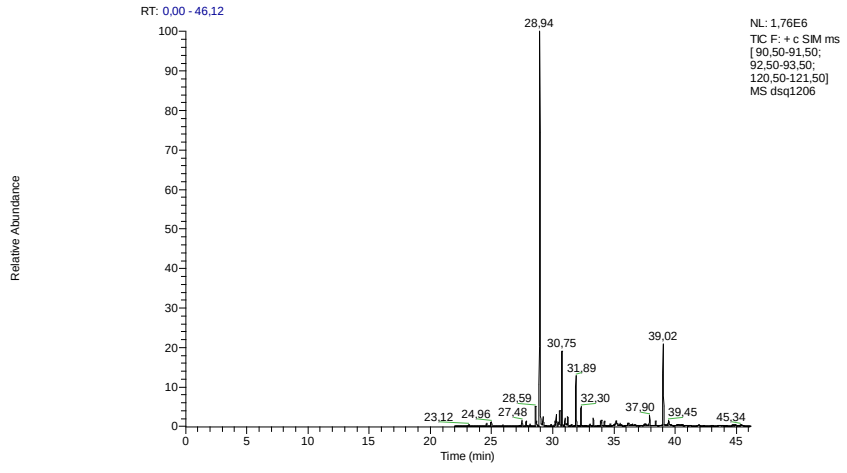


Figure 10: SIM (Selective Ion Monitoring) chromatogram using 91, 93, 121 as detected masses. The highest peak at retention time of 28.94 min is identified as sabinene.

Partner P1 collected the ecophysiological data of the trees grown under controlled conditions. In addition to seasonal sampling, two detailed experiments were performed: (1) study of the impact of varying temperature conditions (2007) and (2) study of the impact of varying soil water content conditions (2008 and 2009) (Figure 11). The data are shown in section WP2.4.

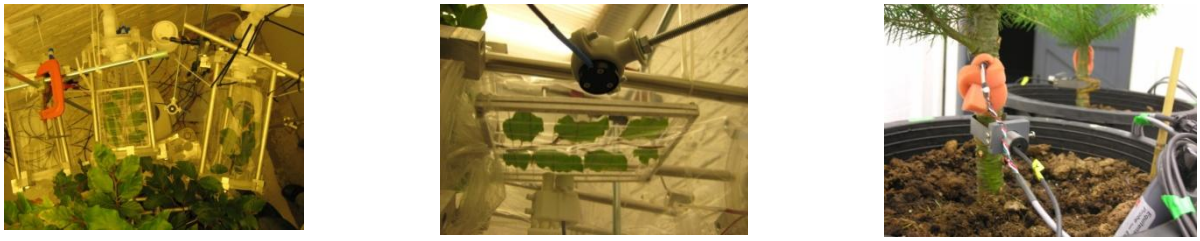


Figure 1: (a) View of branches enclosed in the two measuring cuvettes and of the empty reference cuvette, (b) detail of the grid for horizontal and non-overlapping positioning of leaves (c) LVDT (linear variable displacement transducer), TDP (thermal dissipation probe) installation on conifer tree.

In the first experimental period eight different light intensities were selected, including complete darkness. The light intensity was varied every hour in ascending order starting from 8 h in the morning reaching maximum at 14-16 h. From 16 h on the light intensity was decreased until 22 h, when darkness started (Figure 12a). The following temperatures in the growth room were used: 21 (reference), 23, 25, 27, 29, 31 and 33°C.

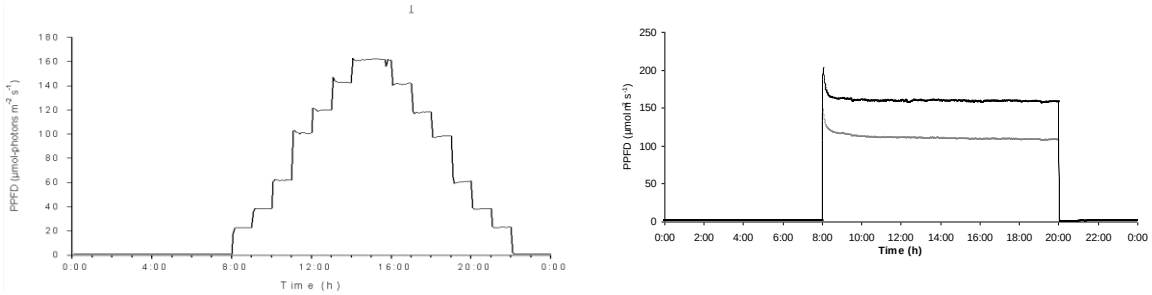


Figure 2: Stepwise variation (a) and one-step (b) PPFD in the growth room simulating the natural daylight in ascending and descending order.

According to the WPs during 2009, the growth chamber experimental set-up as previously designed was used for measurements on two model trees: two *Pseudotsuga menziesii* trees and the drought stress repetition on two *Fagus sylvatica* trees. During the drought stress experiment only one light step was selected (Figure 12b) complete darkness between 20h and 8h, maximum PPFD (300 µmol-photons m^{-2} s^{-1}) between 8h and 20h and the temperature in the growth room was set at 21°C. This was initiated on September 21st 2009 and the stressed beech tree was rewatered on October 12th 2009. Measurements consisted of (1) discontinuous off

line and (2) continuous online data acquisition. The on line measurements included the following variables: stem fluctuations, sap flow, net photosynthesis rate, monoterpenoids emissions (focus on ion signals related to monoterpenoid (*m/z* 81 and m/z 137). Similar measurements continued on *Fraxinus excelsior* in 2009 and in 2010 on *Pinus nigra*.

Stem diameter variations (D) were measured using a linear variable displacement transducer (LVDT, type LBB 375-PA-100 and transducer bridge 8C-35, Schaevitz, Hampton, VA, USA) installed below the TDP at about 20 cm above the soil. A custom-made stainless steel holder was used for fixation of LVDT at the stem level. Continuous measurements of stem diameter variations were used to calculate maximum daily shrinkage (MDS). MDS was computed as the difference between the maximum stem diameter, just before sunrise, and the minimum stem diameter in the afternoon within 1 day (De Swaef et al. 2009). Sap flow was followed at the base of the tree stem (25 cm above soil) with a thermal dissipation probe (TDP-10, Dynamax, TX, USA). In addition, discontinuous online data measurement included measurements of leaf water potential using the Scholander pressure bomb (PMS Instruments, Corvallis, OR, USA), the chlorophyll content index (CCI) using the Minolta Chlorophyll Meter SPAD-502 (Minolta Corporation, New Jersey, USA), net photosynthesis measurement by clamping intact leaves/needles into portable photosynthesis system LICOR (type LI-6400, Lincoln, NE, USA).

2.4 Data analysis

General BVOC emissions patterns

Ion signals related to monoterpenoid (m/z 81 and 137), isoprene (m/z 69) and acetone (m/z 59) emissions have been measured continuously with the PTR-MS during the five experimental periods in 2007. The data show that beech (*Fagus sylvatica* L.) is a low isoprene emitter and a rather strong monoterpenoid emitter. Therefore data-analysis mainly focused on monoterpenoid emissions.
As an example, the monoterpenoid emission rates, calculated based on the m/z 137 PTR-MS ion signal, are shown in the lower panel of Figure 13 for cuvette 1 during period 07 exp p2 and period 07 exp p3. During these periods the beech trees were subjected to a constant daily PPFD pattern (see Figure 12). The variation of the leaf temperature during these experimental periods (as a consequence of the different settings of the growth room temperature) is shown in the upper panel of Figure 13.

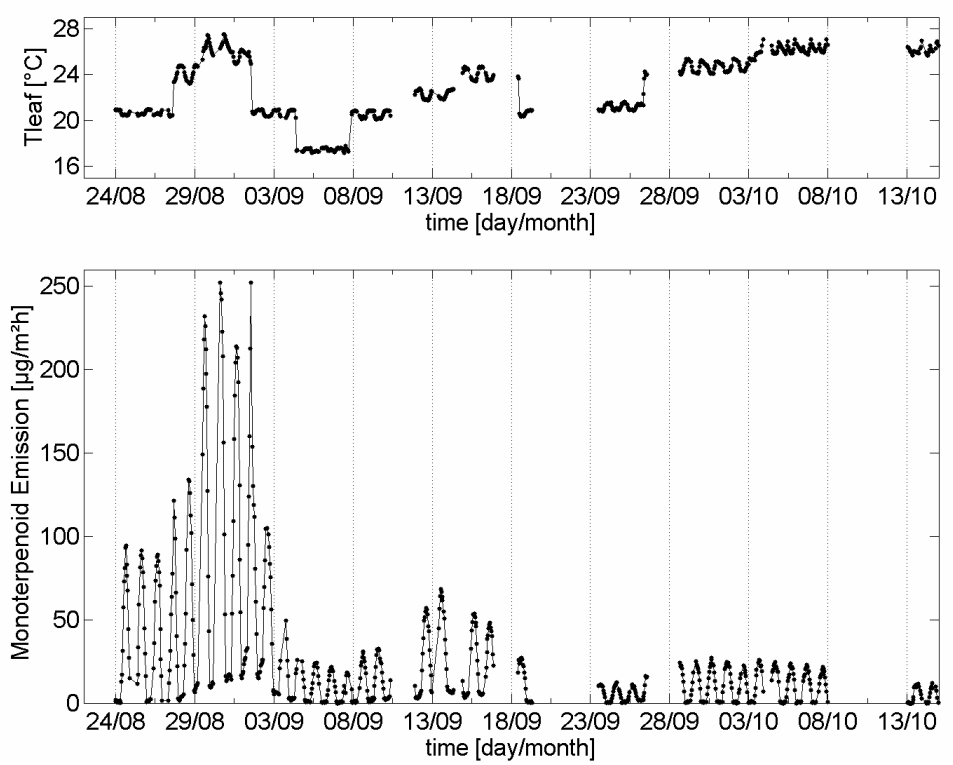


Figure 13: Variation of the leaf temperature during exp p2 and exp p3 2007 (upper panel) and monoterpenoid emission rates (m/z 137) (lower panel).

Leaf infection by mites

During the growth chamber experiment on *Fagus sylvatica* L. (PPFD, temperature controlled) of 2008 (08 exp p1-p4), 33 samples have been analyzed by TD-GC-MS. 16 compounds were detected, including 10 monoterpenes (MT), linalool, (E)-4,8-dimethyl-1,3,7-nonatriene (DMNT), 2 sesquiterpenes (SQT), isoprene and methyl salicylate. Sabinene showed the highest emission, in an agreement with previous studies (Moukhtar et al. 2005; Holzke et al. 2006).

Quantifiable emission appeared 21 days after budburst, and reached the highest level at the beginning of summer. MT emissions showed a clear trend in following each other. As an illustration the trend of sabinene and limonene emission is presented (Figure 14).

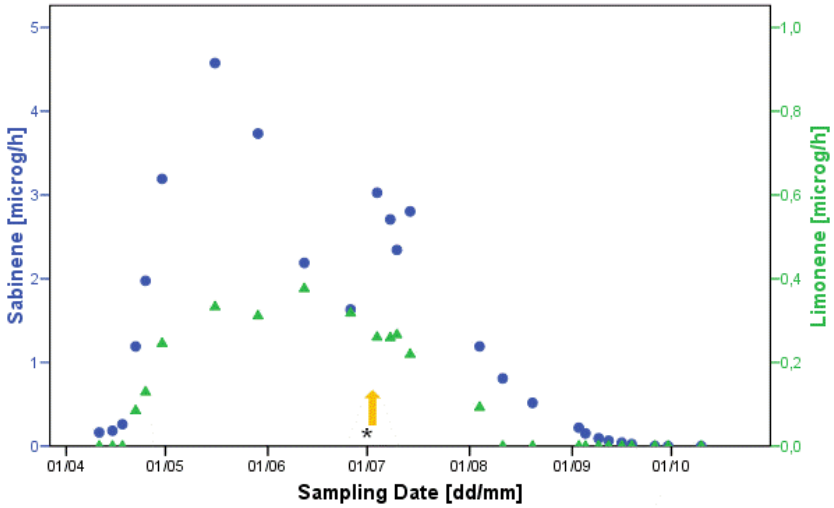


Figure 14: Variation of sabinene and limonene mass flows over a total vegetation period. Experiments were perfomed in the growth chamber and lasted from March to November 2008. PPFD was kept constant from 8 am till 8 pm and temperature was set at 21°C. * Jump in the emission is due to the installation of a new lamp with increased light intensity.

In the middle of autumn phytophaga infection was observed on the tree induced by two-spotted mite (*Tetranychus urticae*). New compounds appeared as a result of infection (linalool, methyl salicylate, (E,E)-α-farnesene, (E)-4,8-dimethyl-1,3,7-nonatriene, unknown SQT) and became dominant over sabinene, explained by the low MT emissions at this time of the year.
These observations point at the importance of further investigation of BVOC emissions (especially SQTs and oxygenated-MTs) and the need for a proper quantification system of these compounds. A peer-reviewed paper on biogenic stress induced emissions has been published (Joó et al. "Variation in biogenic volatile organic compound emission pattern of *Fagus sylvatica* L. due to aphid infection").

Response of BVOC emissions to variations of PPFD at fixed temperature conditions

To see the relationship between BVOC emission and PPFD, samples from ***Fagus sylvatica* L**. were taken at different PPFD levels during the chosen days. The curve obtained is shown in Figure 15 with the conditions of air temperature equal to 27 °C and PPFD in the range from 0 to 150 µmol-photons m^{-2} s^{-1} (data for 31-08-2007).

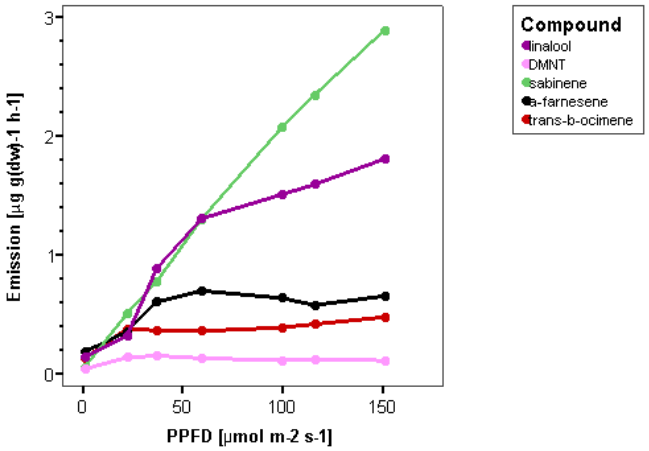


Figure 15: Light response for BVOC emission (different compounds) at 27°C leaf temperature and different PPFD values.

Six compounds were found to be emitted, mostly monoterpenes and one sesquiterpene, identified as α-farnesene. The highest emission is related to sabinene as it was expected from previous results. For sabinene a linear correlation can be seen on the graph with a coefficient of determination R^2=0.996, which is not the case for other terpenes. From full day measurements a difference in emissions, with lower amount in the mornings, was obtained at same conditions as in the afternoons. This effect was observed by Partner P3 as well.
Previously, Kahl et al. (1999) concluded that the contribution of the different sources of intermediates supplying the carbon for the terpene-skeleton varies not only between plant species for a selected molecule, but also within one class of compounds emitted from one plant species. The light dependency experiment carried out on a *Fagus sylvatica* L. under controlled growth room environmental conditions (varying PPFD at a fixed temperature of 21˚C) showed supportive results for Kahl's (Kahl et al., 1999) investigation. One could conclude from Figure 15 that the synthesis of sabinene in the leaves of *Fagus sylvatica* L. is strongly linked to light intensity, but the release of α-farnesene was not influenced by PPFD above ~40 µmol $m^{-2}s^{-1}$. It seems possible that a different minimum light intensity is needed for the production of a steady-state release of particular molecules. Besides, the night-time emission of α-farnesene (after 10 h of darkness) suggests existence of storage pools for SQTs in the leaf of *Fagus sylvatica* L.

Out of 48 samples taken from two ***Pseudotsuga menziesii*** (1 and 2), isoprene, α-pinene, sabinene, β-pinene, 3-carene and limonene could be accurately quantified. The two pinenes comprised 70% of total terpene emissions in which the proportion of α-pinene was slightly higher than that of β-pinene.
The relationship was examined between the mass flow of terpenes from the leaves of the young *Pseudotsuga menziesii* 2 and the driving variable light intensity. The stepwise variations in PPFD level, ranging from 0 to 175 µmol photons m^{-2} s^{-1} were

investigated at several set point temperatures. The experiments with altering light intensity performed at constant leaf temperature, indicated that biogenic volatiles were not strongly affected by light intensity. The mass flows were measured at a mean leaf temperature of 26.87 ± 0.54°C. A repetition of the PPFD-curve was performed at an average temperature of 22.73 ± 0.37°C (Figure 16). As shown by the graph, the mass flow of the five identified monoterpenes was significantly above zero during darkness and they exhibited a similar influence by irradiation. Moreover, the variation of the emitted quantity subjected to altering light intensity was rather small, implying a more or less constant release for each of the monoterpenes.

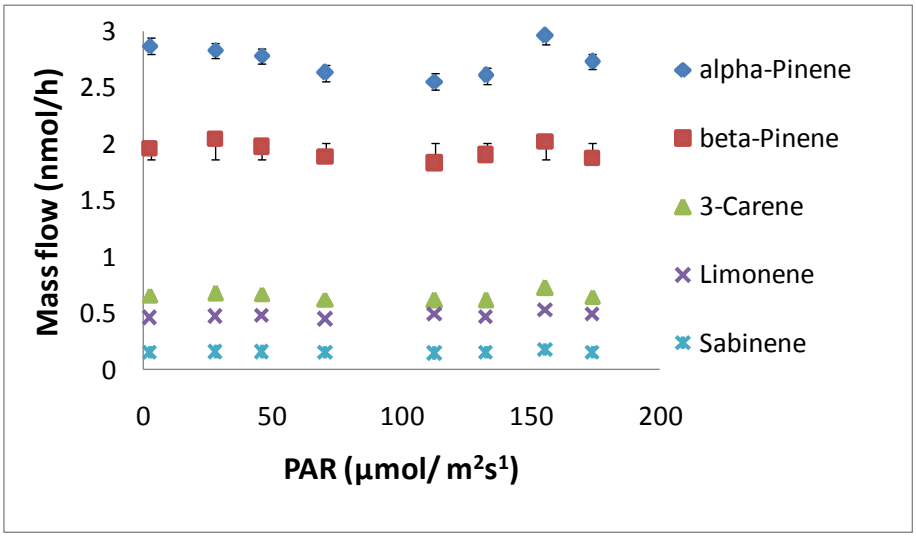


Figure 16: Light responses of monoterpene emissions to different PPFD levels at air temperature of 22.73 ± 0.37°C. The experiments were performed on 20 April 2009.

Summarized, significant emissions of monoterpenes were found during night time measurements and a clear light dependence of its emission rates could not be detected for the Douglas fir. More information on the emissions of Pseudotsuga menziesii can be found in Joó É. et al. Constitutive versus heat and biotic stress induced BVOC emissions in *Pseudotsuga menziesii* (Atmospheric Environment 45, 2011).

Temperature dependence of BVOCs from Pseudotsuga menziesii

In order to study the response of the emissions on variations in temperature, the temperature was altered stepwise. Before going to a next temperature, the emissions should be stabilized at the set point temperature for at least one day. Temperature ranged from 19 to 33°C and its influence was respectively observed at the maximum PPFD level, respectively 137 µmol m^{-2} s^{-1} and 175 µmol m^{-2} s^{-1}.
The temperature was set to a reference temperature of 21˚C on 9 April and 22 April, respectively. As shown by Figure 17, there is a large differentiation in the mean released quantity of BVOC during the experimental period, with highest emission on 9 April.

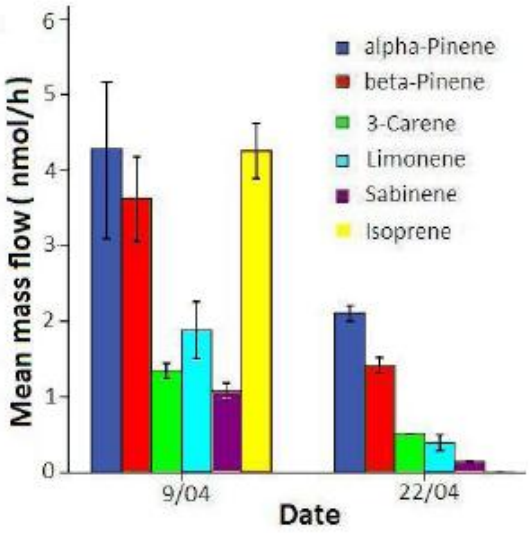


Figure 17: Mean emission of the emitted compounds from Pseudotsuga menziesii 2 at the reference temperature (21°C), respectively on 9 April (n=3) and 22 April (n=3). Error bars represent the 95% confidence interval.

A detailed overview of the temperature effect of monoterpene emission rates after the observation of budburst is shown in Figure 18 along with regression fits to the data. The released quantity of several monoterpenes of the first tree species increased exponentially with temperature. Moreover, the coefficient of determination, R^2, pointed to an exponential relationship between temperature and emitted quantities. This relationship was detected for the principal compounds, respectively α-pinene, β-pinene, limonene and sabinene. A clear link between temperature and the mass flow of 3-carene was not determined.

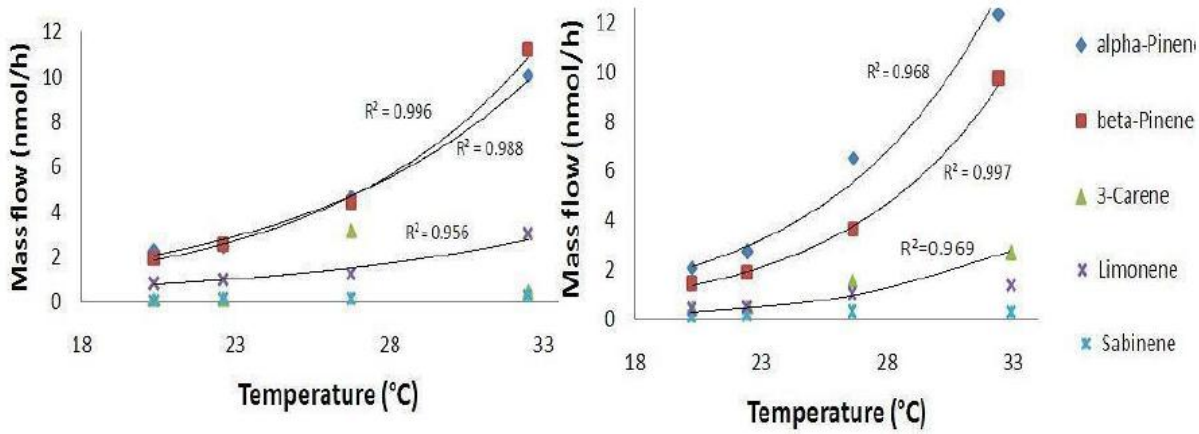


Figure 18: Effect on temperature on the monoterpene emission rates after observation of budburst. The left graph presents Pseudotsuga menziesii 1 and the right graph shows Pseudotsuga menziesii 2. R^2 illustrates the regression fit of the data.

Integration of BVOC emissions and photosynthesis at various temperatures

The impact of temperature variation from *Fagus sylvatica* L. was studied in the period 07 exp p2. Temperature was constant during the day, and varied from 17-27°C between days. The daylength in the growth room was 14 h, representing the mean daylength of June/September months. Moreover, this intermediate photoperiod was optimal for obtaining vigorous vegetative growth. The transition days (when temperature was changed) were not taken into account in the analysis, unless specified. Days with electricity problems or instrumentation problems were removed from the analysis. The temperature variation applied was random. A temperature of 21°C was taken as reference temperature, because a beech temperature optimum of net CO_2 assimilation was found to be around 21°C in previous experiments.
Mean diurnal patterns for each temperature were calculated for photosynthesis and monoterpenoid emissions. Pronounced diurnal dynamics were observed (Figure 19). A clear link was observed between temperature variation and the monoterpenoid emissions. When the tree was exposed to higher temperatures (up to 27°C), monoterpenoid mixing ratio was higher. At 27°C emissions reached a peak value of 257 µg m^{-2} h^{-1}. Thus, the monoterpenoid flux was enhanced almost 5 times higher during the period of higher temperature exposure compared to the reference temperature of 21°C. Monoterpenoids did not exhibit a temperature optimum (within the range of 17-27 °C). The response of monoterpenoid emissions was dramatically attenuated when exposing the tree to lower temperatures. At temperatures of 17°C, peak emissions obtained were only 24 µg m^{-2} h^{-1}. However, the net photosynthesis appeared not to be affected by the temperature range used in the experiment. This indicated optimal conditions for photosynthesis. The net CO_2 assimilation maximum ranged from 5.22 to 6.26 µmol m^{-2} s^{-1}, between 14 and 16 h when intensity was highest. The negative values of the CO_2 assimilation during darkness indicated dark respiration.

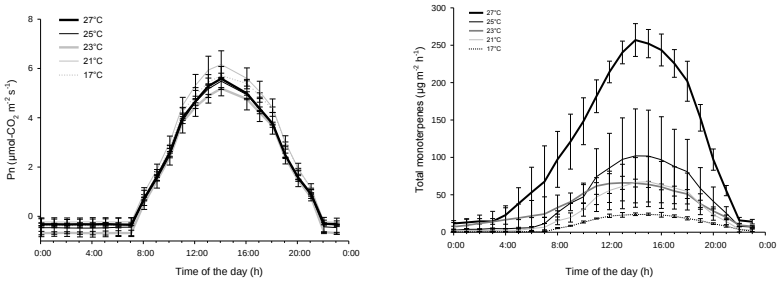


Figure 19: (a) Mean diurnal patterns of net photosynthesis for each imposed temperature. Negative values represent the night-time dark respiration. (b) Mean diurnal patterns of monoterpenoids for each imposed temperature. Low night-time emissions were observed.

Net photosynthesis rates and monoterpenoid emissions showed pronounced diurnal dynamics as the lights were gradually switched on/off. The fraction of assimilated C re-emitted back to atmosphere through monoterpenoid emission was represented by the

C ratio between PTR-MS total emitted monoterpenoids and the net photosynthesis. The results revealed that the potted beech tree under well-watered conditions re-emitted a rather low fraction of the assimilated carbon back into the atmosphere as total monoterpenoids. This fraction increased from 0.01 to 0.10 % with a temperature rise from 17°C to 27°C in growth room conditions (Figure 20). This MT/Pn ratio clearly showed an exponential increase with increasing temperatures. We obtained the following relationship: y = 0.003 * exp (0.2149 * x). The coefficient of variation (R^2) was 0.8749 (*P*-value < 0.01).

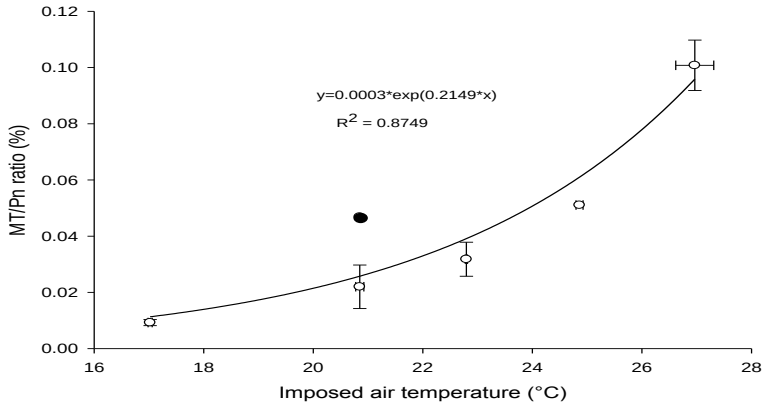


Figure 20: Exponential relationship of the total monoterpenoid/net photosynthesis (MT/Pn) ratio in function of temperature. Temperature transition days are not included. The full black circle represents the ratio measured the day after transition from 27 to 21°C. This day is not included in the mean value for 21°C.

The full black dot in Figure 20 represents the day after temperature was changed from 27 to 21°C. The beech leaves needed a 1-day adaptation time and showed a higher calculated ratio compared to other days of 21°C. Therefore, this day was considered as an outlier, and was not included in the calculation of the mean value. A peer-reviewed paper on these experimental results is published (Šimpraga et al. "Comparing monoterpenoid emissions and net photosynthesis of beech (*Fagus sylvatica* L.) in controlled and natural conditions").

Drought stress experiment

Up till now it is known that BVOC emissions are driven by light and temperature. Regarding drought effects, literature is conflicting. Some authors indicate that drought stress enhances (Sharkey et al. 1993), while others say it reduces the emissions (Bertin et al. 1996). As drought is worldwide the most significant limiting factor for plant growth, a combination of plant metabolic processes and abiotic drought stress was investigated. Bio-sensors were used to yield extra information on the physiological status of the model trees. The objectives were (1) to investigate the effect of drought stress on BVOC emissions and (2) to relate the BVOC emissions to some main ecophysiological plant processes (i.e. net photosynthesis, internal water transport,

stem diameter variations). The results are shown in Figure 21. From the results we can see that monoterpenoid emission was linked with tree physiology; more specific with leaf net photosynthesis rate, with stem diameter growth and with sap flux density as well as an interdependence between leaf and tree plant processes was observed. Imposed severe drought caused Pn and MT emissions to decrease. Upon Pn inhibition, the emission of MT is inhibited most likely due to the photosynthetic origin of the MT.

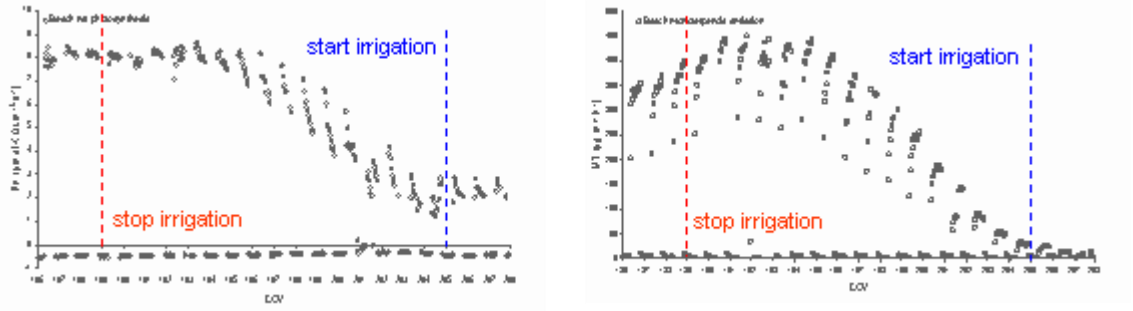


Figure 21: Leaf-level processes measured on beech during the drought stress experiment: photosynthesis (left) and monoterpenoid emissions (right).

Severe drought stress limited and had a negative effect on the overall tree physiology as well as on the monoterpenoid emissions. Stem diameter growth indicated a decrease in stem growth, while sap flux density almost completely stopped (Figure 22). After re-watering a sharp increase in stem diameter growth was observed followed by a slight increase in sap flux density. After re-watering MT emissions did not recover, while Pn slightly recovered. In the end, one can conclude that drought stress limitation on these processes might become significant in changing global climate conditions.

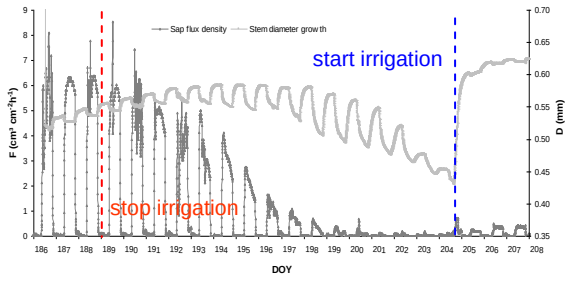


Figure 22: Tree-level processes (sap flow, stem diameter variation and leaf water potential) during the drought stress experiment showing decrease in tree processes and recovery upon re-watering.

WP3 Canopy experiment

3.1 Branch cuvette

The branch cuvettes that were used for the canopy experiment in the Aelmoeseneie forest are of similar design as the ones used in the growth chamber experiments, except that they are somewhat larger. Most components of these cuvettes have been manufactured by the mechanical workshop of Partner P3. The plexi glass base plates and three support rings were manufactured by a specialized company. The robustness of the cuvettes in real outdoor conditions and of the experimental set-up has been tested in December 2007 before the start of the measurement campaign in the Aelmoeseneie forest (paragraph 3.2).

3.2 Experimental set-up gas exchange

The canopy experiment was conducted in 2 large measurement campaigns (Table).

Table 4: 2008 experimental scheme of IMPECVOC 2008 campaigns in the Aelmoeseneie experimental forest.

Experiment campaign 1 (08 exp c1)	Experiment campaign 2 (08 exp c2)
26/05/08 – 26/06/08	04/08/08 – 01/12/08

Preparatory activities for the 2008 campaign were performed in the fourth trimester of 2007 by Partner P3, such as the installation of insulated heated outlet lines (PFA) and several electrical cables from the third floor (22.5 m) of the measuring tower to the log cabin in the Aelmoeseneie forest, of connection boxes (for a pump, fans, flow meters, micrometeorological sensors), of an ADSL line (for remote communication with the instrumentation) and of an air-cooling unit in the log cabin. To avoid practical problems at a later stage (e.g. related to power consumption, temperature control in the log cabin, remote communication with the analytical instrumentation, heating of the outlet lines, robustness of the branch enclosure systems during bad weather conditions, …), performance tests of the complete experimental set-up under real outdoor conditions were performed in December 2007. During these tests a branch of a solitary potted coniferous *Pseudotsuga menziezii* [Mirb.] Franco tree, located on the third platform, was enclosed in a prototype 27 litre cuvette, manufactured in the mechanical workshop of BISA. A second identical, but empty, cuvette was installed close to the first one to determine possible background emissions. PTR-MS, IRGA

and gas sampling for off-line GC-MS analysis were carried out simultaneously and no major technical problems were encountered.

During the first five months of 2008 the installation in the forest was completed by Partner P3. From the measuring tower branches at different heights in the canopy of an 80 years old *Fagus sylvatica* L. tree are accessible. Six identical cuvettes were installed: 2 branch cuvettes and 1 reference cuvette on the third platform (22,5 m), 1 branch cuvette and 1 reference cuvette on the second platform (15 m) and 1 branch cuvette on the first platform (7.5 m) (Figure and Figure). All cuvettes were equipped with a thermistor (to measure air temperature) and a relative humidity sensor. All branch cuvettes were also equipped with an IR-thermocouple (to measure leaf temperature) and PAR sensors (2 per cuvette on the third platform, 1 per cuvette on the other platforms). Two systems for VOC- and ozone-free air supply to the cuvettes were installed as well, identical to the one used in the growth chamber.

The IRGA of Partner P1 was coupled with the multiplexer of the PTR-MS analysis circuit in order to allow simultaneous measurements of net photosynthesis and transpiration rate.

Figure 23: Experimental set-up at the Aelmoeseneie tower on the 3rd and 2nd floor.

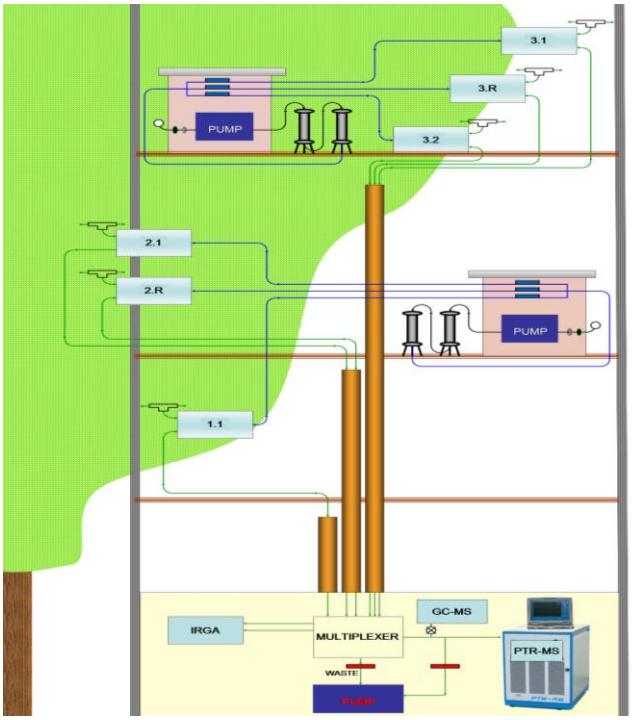


Figure 24: Schematic representation of the experimental set-up in the Aelmoeseneie forest.

In the Aelmoeseneie forest in 2008, CO_2 and H_2O gas flux measurements from the canopy were performed by the characterisation of the different canopy layers *in situ* using two types of IRGAs (Figure 23 and Figure): (1) a stationary gas exchange measuring system IRGA ADC 2250, an NDIR analyzer (Non-Dispersive Infra-Red) operating in the differential mode under steady-state conditions and (2) a portable gas exchange measuring system IRGA LI-6400 equipped with LED (Light Emitting Diodes) light source operating under set environmental conditions. Both systems' calibration were performed manually by passing a known CO_2 concentration through both the reference cell and the analysis cell simultaneously. The gas exchange was measured in the sun-layers and the shade-layers of the canopy including all 3 tower platforms. Data of stationary IRGA were continuously recorded at 1-min intervals. Leaves were measured at ambient CO_2 concentrations.

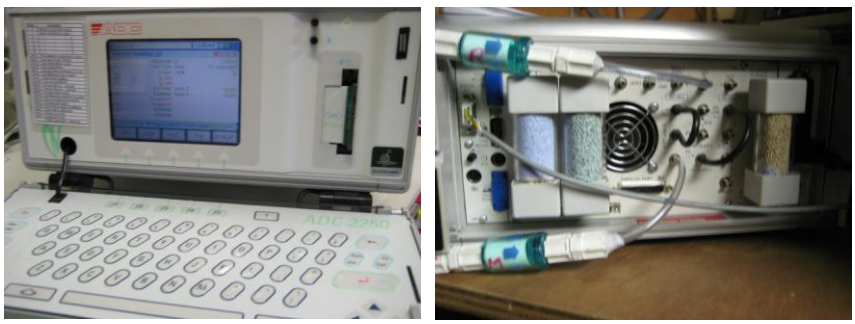


Figure 23: Stationary ADC 2250 IRGA to measure online photosynthesis and transpiration rates.

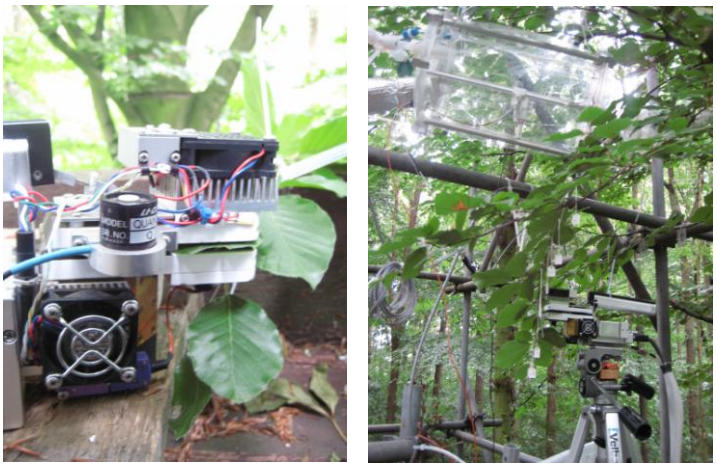


Figure 26: Portable LI-6400 IRGA in the Aelmoeseneie forest (9 July 2008) to measure offline photosynthesis and transpiration rates

3.3 Canopy measurements during different phenological phases

PTR-MS measurements were started on May 7th 2008 in the Aelmoeseneie forest and IRGA measurements on May 26th 2008. Continuous PTR-MS and IRGA measurements went on until June 26th 2008. On June 26th the PTR-MS was moved to the growth chambers to be included in the drought stress experiments. Continuous measurements in the Aelmoeseneie forest were resumed on August 8th until November 28th 2008. On a regular time scale samples for GC-MS analysis were collected by Partner P2. Measurements from the two branch cuvettes on the third platform (horizontal scan) should allow us to study the branch-to-branch intervariability of BVOC emissions and of CO_2 and H_2O vapour exchange at the same altitude level in the canopy of the adult beech tree. Alternate measurements from branch cuvettes at the different platforms (vertical scan) should result in information on the emissions as a function of the vertical position of the branches in the canopy (sunlit versus shaded leaves). Horizontal scans during one day have been alternated by vertical scans the next day.

3.4 Data analysis

Ion signals related to monoterpenoids (m/z 81 and 137), isoprene (m/z 69), acetone (m/z 59), acetaldehyde (m/z 45), methanol (m/z 33) and water (m/z 39) have been measured continuously with the PTR-MS during the measurement campaign in the forest Aelmoeseneie. The huge amount of PTR-MS measurements and of micrometeorological data has been stored by Partner P3 in an extensive database, which is accessible for the different partners in the project. As an example of the data analysis, the calculated monoterpenoid emission rates for cuvette 3.1 (third

platform, sunlit leaves) are shown in Figure for the months August and September 2008.

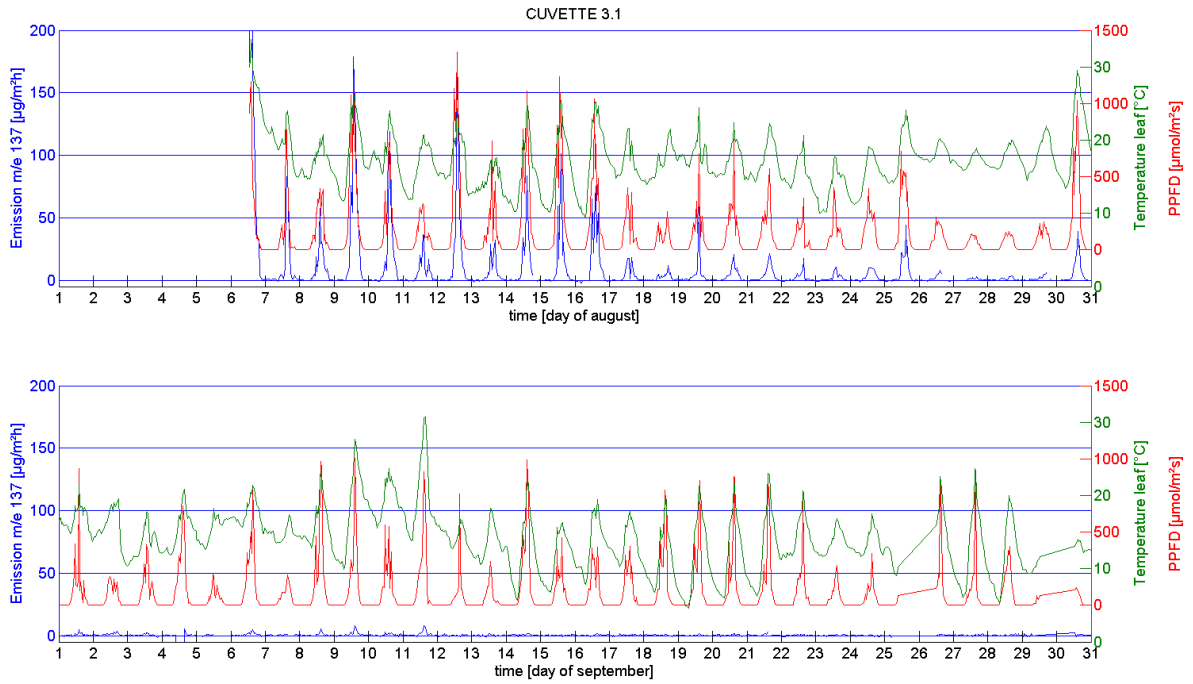


Figure 27: Blue: calculated monoterpenoid emission rates for a sunlit branch at a height of 25 m in the canopy of an 80 years old beech tree during the months August and September 2008. Red: the variation in PPFD. Green: the variation of the leaf temperature during these months.

The relation between photosynthesis and BVOC emission within the canopy was analysed in detail. This work resulted in two publications. A first publication compares the behaviour of sun and shade leaves (Bloemen et al. “How do sun and shade leaves in European beech (*Fagus sylvatica* L.) influence volatile organic compounds emitted into the atmosphere? To be submitted”). A second publication analyses the vertical gradients that were observed during the canopy experiment (Šimpraga et al. “Vertical gradient of photosynthesis and monoterpenoid emissions in a beech canopy under different sky conditions” to be submitted).

WP4 Stand level experiment in Vielsalm

4.1 Preparation experimental site

The operational infrastructure needed at the Vielsalm forest site includes a meteorological tower fully equipped with adequate sensors, and an equipped shelter. The existing set-up had to be strongly updated for BVOC measurements.

Tower

The boundary layer theory specifies that, in the first hundred meters of the atmosphere the size of eddies (which are the main responsible transport entities) increases with height. As a consequence, the concentration fluctuation frequencies measured by an eddy covariance system are higher close to the surface. The tower height of the Vielsalm site was chosen in order to comply with these constraints and the IRGA (CO_2 and H_2O analyser) performances. As the PTR-MS analyser is characterized by a lower acquisition frequency, this constraint was no more satisfied and it was expected that the loss of signal in the high frequency range would be too important to allow reliable BVOC measurements. In order to solve this problem, it was necessary to increase the tower height. One consequence would be an enlargement of the system footprint. However, this problem was not critical as the fetch (distance between the tower and the forest edge) in the two dominant wind directions (SW and NE, respectively) was large enough to ensure that the footprint would still be inside the target ecosystem. The present tower has thus be replaced by a new one of 50m height using funding obtained from Belgian national agency (FNRS) (Figure).

Shelter and basic equipment

A new and bigger shelter has been built and equipped close to this tower to allow the hosting of the PTRMS analyser in the beginning of phase II. The installation of additional power lines and communication tools were necessary to upgrade the remote control of the instruments which is crucial for the continuity of the BVOC measurements.

Sensors

The tower has been re-equipped with an extensive set of meteorological sensors. We took this opportunity to upgrade the whole site installation that was running continuously since 12 years. Additional sensors have also been installed in the frame of other projects. Dry and wet nitrogen deposition measurements are now performed and an NDVI sensor has been installed on the top of the tower that allows a qualitative monitoring of the state of vegetation. Sapflow measurements together with measurements of the profile of soil moisture have started in the 2009 summer. Litter fall bags have also been installed. All these devices will allow better analysing the responses of BVOC fluxes to climate, season and phenology.

Tubing

The tubing for BVOC as well as for CO_2 and H_2O sampling above the forest have been installed in insulated and heated protections. Beforehand, the computation of the aerodynamic requirements have been performed in order to select optimal system dimensions (pumping rate, tube size and filter characteristics) taking PTR-MS constraints (inlet pressure, response time) into account. This was made in collaboration with Partner P3.

Figure 28: Left: the new shelter and the bottom of the new tower. Right: the new tower equipped with tubing for BVOC sampling at the top of the tower (orange tube).

4.2 Preliminary tests

Operational coupling of PTR-MS to eddy-covariance set-up

Computation of eddy covariance flux requires treatment of several hundred thousands data per half hour. In the absence of a ready-to-use logging system, an interface and logging software, that allows data acquisition, storage and treatment, have been realized. The software collects and synchronises high frequency datastreams coming from the sonic anemometer and the PTR-MS and performs the flux computation. We decided to log the datastreams from the two instruments on a single computer. This logging strategy presents three major advantages. (i) a single computer being used, perfect synchronisation between the two datastreams is guaranteed, this point being crucial for the flux computation. (ii) the EC-BVOC logging system is completely independent of the traditional CO_2-H_2O eddy-covariance set-up and of the proprietary logging system of the PTR-MS, allowing a better flexibility. (iii) this flexibility will allow handling of complex PTR-MS sequences in avoiding complicated post-processing of data, the number of scanned masses and the integration time for each mass being taken as parameters of the logging system.
A logging test in real conditions was realized in early June 2008 in situ at the Aelmoeseneie site (Figure). The aims of this test were (1) to assess the quality of our acquisition system and (2) to obtain real raw data to test the data treatment tools that were under development.
The sampling sequence of the PTR-MS is given in Table giving a total cycling time of 1.8 s. This sequence and the choice of compounds is very close to what was done routinely in Vielsalm during the phase II of the project. A sonic anemometer (Young

81000) was installed above the canopy, at the top of the tower (35 m) and was run with a 16 Hz sampling frequency. A PTR-MS sampling line (PFA tubing of 6.4 mm inner diameter) was extended from the third floor and air was drawn to the PTR-MS with a 9 l min^{-1} flow rate from an inlet placed close to the sensing volume of the sonic anemometer. The system was run during a whole hot and sunny day, giving eleven half-hours of usable synchronised raw data.

Figure 29: Left: sonic anemometer installed at the Aelmoeseneie forest. Right: logging of EC-BVOC data.

Table 5: Description of the PTR-MS sequence during the eddy-covariance test on 09/06/2008.

Compound	Product ion mass [amu]	Dwell time [s]	Calibration factor [ncps/ppbv]
H_3O^+ Primary ion	21	0.23	-
Oxygen	32	0.23	-
Water cluster	39	0.23	-
Acetaldehyde	45	0.23	-
Acetone	59	0.23	19.098
Isoprene	69	0.23	6.9598
Monoterpene fragment	81	0.23	5.6694
Sum of monoterpenes	137	0.23	3.95

Fluxes and mixing ratios of compounds for which calibration factors were available are given in Figure . The error bars represent the detection limits computed, following Spirig et al. (2005), as the standard deviation of the covariance function in a time-lag window far away from the true lag. This quantity corresponds to the lag-independent noise in the covariance function. Despite important detection limit ranges, an obvious dependence of the fluxes on PPFD was found for isoprene and monoterpenes, indicating reliability in the data acquisition and the flux computation.

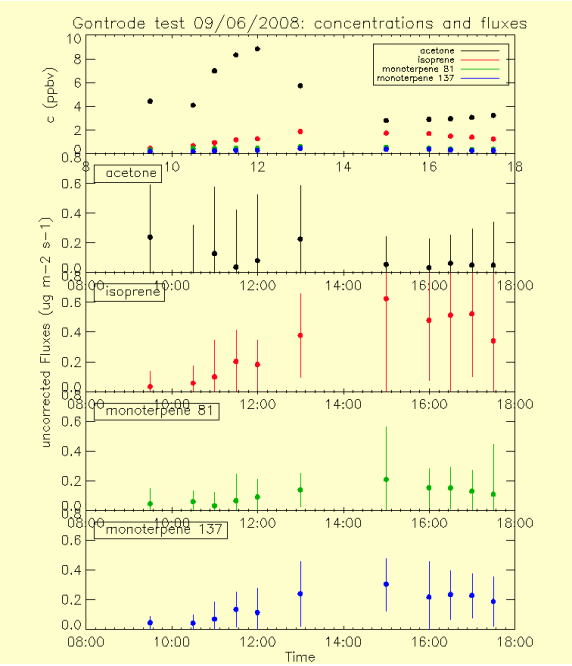


Figure 30: (a) BVOCs mixing ratios as determined from PTR-MS measurements. (b-c-d-e) Fluxes of BVOCs. These fluxes are not corrected for high-frequency damping. Error bars are the precision of individual flux measurements.

Methodology of flux computation

An extensive bibliographic research on eddy-covariance BVOC measurements has been made and contacts with experts have been established in order to identify the methodological problems specific to eddy covariance measurements of BVOC fluxes and to consider the solutions that have been brought.

In particular, the method called “virtual disjunct eddy covariance” (vDEC) was identified as the most appropriate to BVOC fluxes. Rather than using high frequency concentration and velocity measurements as EC (around 10Hz), this method sub-samples the data series at lower frequency, pairing-up each concentration measurement with the associated wind measurement. This allows working with lower frequency analysers and, in the case of BVOCs, to scan a larger spectrum of components at the price of a limited information alteration.

However, the flux quality alteration depends on the spectral content of the turbulence which can be site-specific. In addition, different vDEC procedures have been proposed in the literature. We thus developed a data analysis in order to test the impact of disjunct analysis on the Vielsalm data. To this end, the existing time series obtained with conventional EC for CO_2/H_2O were used and artificially resampled in order to simulate the effect of a vDEC treatment (Figure). Comparison with these results and original EC fluxes is used in order to optimise the acquisition software in finding the best compromise between the quality of the flux and the number of masses that are scanned. Results shown in Figure suggest almost no alteration of the fluxes for a disjunct time interval of 1 s (1 Hz), this time interval being representative for a scan on 5 masses, a situation that seems realistic for a long-term run of EC-BVOC above a forest. This situation will even improve due to the increase of the measurement height during the BVOC measurement campaign at the Vielsalm site (new tower), allowing the possibility to increase the number of compounds studied.

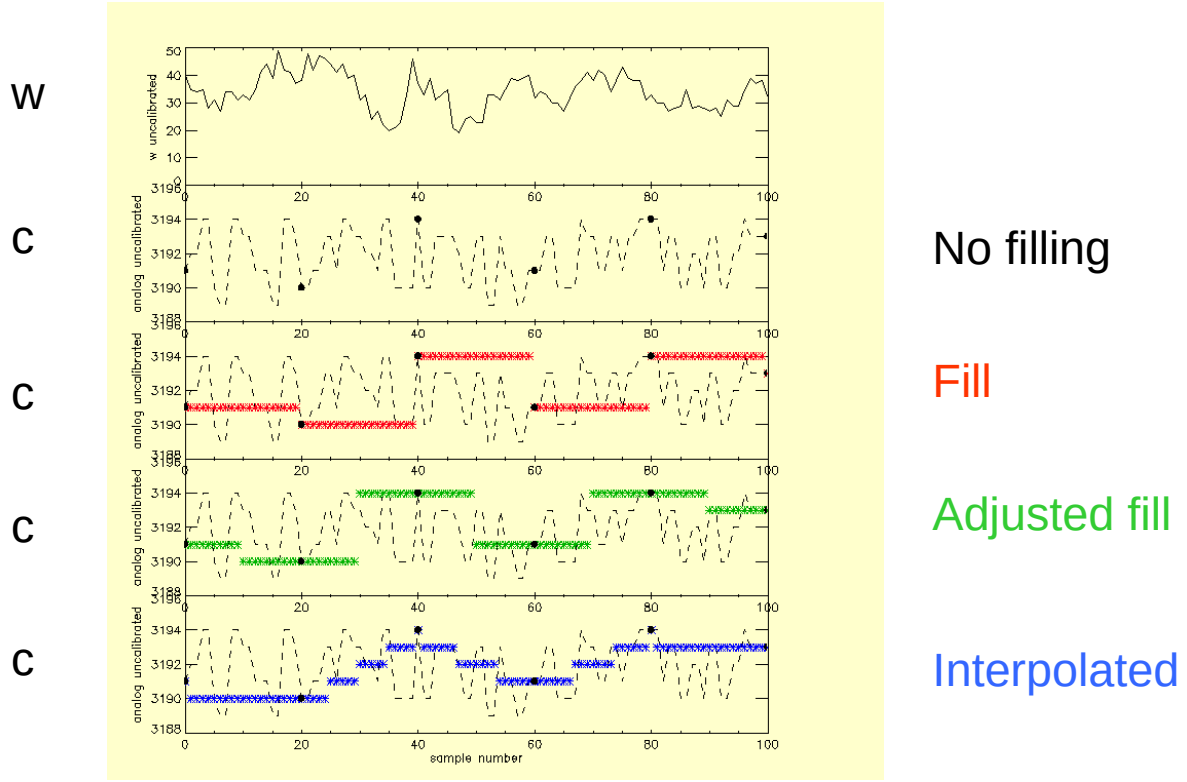


Figure 31: Case example of high frequency CO_2 eddy-covariance data (solid black for vertical wind speed component and dashed black for CO_2 concentration) together with different artificial sub-sampling procedures.

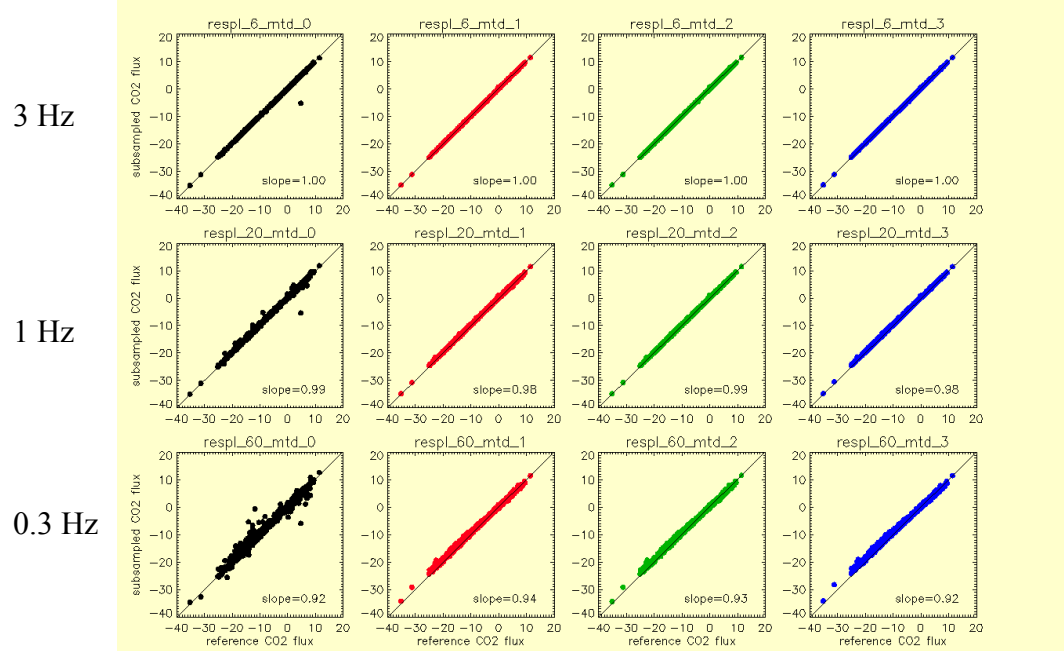


Figure 32: Comparison of the CO_2 flux, subsampled with different procedures, to the reference CO_2 flux computed with the non-subsampled high frequency dataset. This test is performed for three subsampling frequencies.

Another major point for accurate estimation of BVOC fluxes is to be able to correct for damping of fluctuations in the sampling tube. Indeed, a part of the turbulent signal is lost during the transport of the air from the sampling point to the analyser due to air mixing in the filters and the tube. This part of the signal can be recovered through application of correction factors deduced from spectral analysis. Partner P4 has investigated this problem for water vapour using data from Vielsalm (Deligne et al., 2010, “New transfer functions for correcting turbulent water vapour fluxes”, Boundary-Layer Meteorology) and proposed new transfer functions to deal with the damping of fluctuations. This study has been useful for BVOC flux measurements because the same methodology has been applied to derive correction factors for vDEC of BVOCs.

4.3 BVOC eddy-covariance measurements

The 4.3 workpackage activities and report have been done in collaboration between Partner 3 (BIRA) and Partner 4 (FUSAGX).

The Vielsalm experimental site has been completely upgraded at the end of PhaseI-beginning of phaseII of the project. A new 52m height tower has been installed in June 2009. Increasing the tower height was important in order to reduce the high frequency content of the turbulent signal and thus allow a reduced sampling frequency (below 1 Hz) that is inherent to the use of the PTR-MS and the disjunct

eddy-covariance method. A new and bigger shelter, able to host the PTR-MS analyser has been built and equipped, power lines have been added, tubing on the tower has been installed and an extensive set of meteorological sensors (Figure) were installed at the top and along the tower.

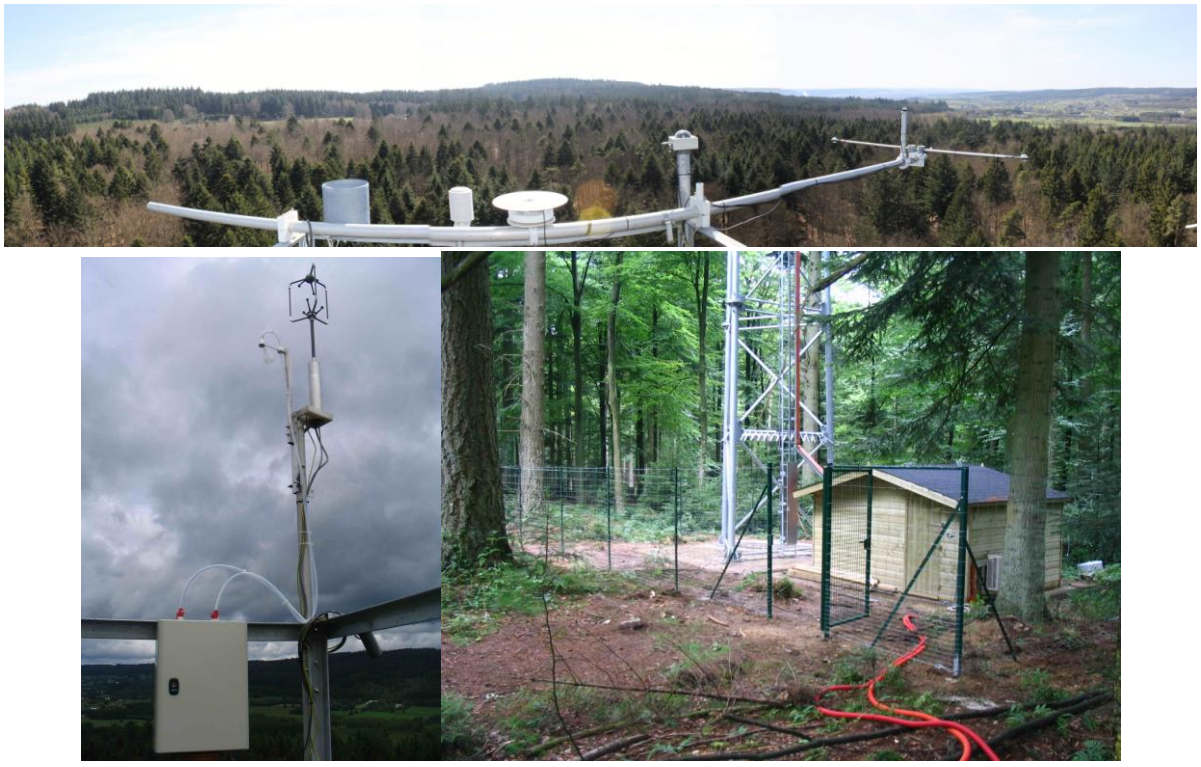


Figure 33: (a) Panorama at the tower top showing radiation sensors (b) the air sampling inlet close to the sonic anemometer (c) the tower base with the shelter hosting the PTR-MS and acquisition systems.

Routine measurements of BVOC fluxes started on July 10th 2009 and ran smoothly until November 17th 2009 (131 days) when the PTRMS went back to the lab. In 2010, measurements started on March 26th and ended on November 18th (236 days). We had an overall BVOC flux data coverage of 83% during these periods, which is a very nice performance for such a complex system and in outdoor conditions. Data gaps were due to power cuts and problems with the source or the detector of the PTR-MS, maintenance and calibration of the PTR-MS. Thanks to the preliminary tests performed during phase I of the project, the coupling and synchronisation of the PTR-MS with the sonic anemometer worked properly. In 2011 the measurements started at April 11th and are still ongoing.

In addition to the PTR-MS reactant ion species (H_3O^+ at m/z 21and $H_3O^+.H_2O$ at m/z 39), ten ion species representative of BVOCs and listed in Table 6 were selected for routine measurements. The ion signal at m/z 87 was followed because it is typical for C5 alcohols, which might interfere with the detection of isoprene, since these are known to have an important fragment ion at the same m/z value of protonated isoprene (m/z 69) (Demarcke et al., 2010). Comparison of measured fluxes and concentrations calculated from the ion signals at m/z 69 and 87, however, indicate

that there is no important contribution of C5 alcohols to the ion signal at m/z 69. Indeed, nice diurnal flux profiles were obtained from the ion signal at m/z 69, whereas no fluxes were observed for the ion signal at m/z 87. Consequently, the ion signal at m/z 69 is expected to be mostly (if not entirely) due to isoprene.

Table 6: Description of the PTR-MS sequence in Vielsalm (Formic and Acetic acid were added in 2010).

Compound	Product ion mass to charge ratio m/z	Dwell time [s]
Methanol	33	0.2
Acetaldehyde	45	0.2
Formic acid	47	0.2
Acetone	59	0.2
Acetic acid	61	0.2
Isoprene	69	0.2
MVK+MACR	71	0.2
Monoterpene fragment	81	0.2
Unindentified compounds	87	0.2
Sum of monoterpenes	137	0.2

Background measurements for the different ion species were obtained every four hours and the PTR-MS was calibrated for the main target compounds (isoprene, sum of monoterpenes, methanol, acetone, MVK+MACR and acetaldehyde) every two to four days (see WP 1.4). Additional features in the logging system were implemented to handle automatically these calibration events in order to improve automatic data treatment.

The sampling sequence of the PTR-MS used a dwell time of 200ms for each ion species, ending in a total cycling time of 2.4s, thus a sampling frequency of 0.42 Hz per compound. Previous tests made with Vielsalm CO_2 datasets showed that reducing the sampling frequency to such values does not alter severely the computed flux.

The computation, correction and filtering procedure of the fluxes have been established and applied. We would like to highlight two important steps in this procedure. First, a major point for accurate estimations of BVOC fluxes is to be able to correct for damping of fluctuations in the sampling tube. Indeed, a part of the turbulent signal is lost during the transport of the air from the sampling point to the analyser due to air mixing in the filters and the tube. This low-pass filter effect can be important for long tubes as it is the case for Vielsalm, because the PTR-MS must be located at the bottom of the tower and the tower is 52m high. This part of the signal can be recovered through application of correction factors deduced from spectral

analysis. This spectral analysis has been extensively performed on our dataset. A consistent cut-off frequency around 0.015 Hz was found at least for isoprene and monoterpenes. The transfer function of the system combined with the spectral content of the signal for the Vielsalm site ends up with flux correction factors comprised between 1.22 and 1.76 for wind speeds equal to 1 and 5 m s^{-1} respectively (mean wind speed is 2.9 m s^{-1}). These correction factors stayed in an acceptable range thanks to the high flow rate in the sampling tube and to the important distance between the sampling point and the top of the canopy reducing thereby the high frequency content of the atmospheric signal.

Another important step comes in the data filtering part. A wood panel factory is located 3.5 km away from the tower in the South-West direction which is the main wind direction. Influence of this factory has never been detected for CO_2 or H_2O flux measurements in the past but this factory can emit very high quantities of BVOCs compared to the forest which is not necessarily the case for CO_2 or H_2O. Indeed, an influence of the factory on monoterpenes, methanol, acetone and acetaldehyde concentrations and fluxes was found (data not shown). These events have to be filtered out of the dataset with a more efficient sorting criteria than the wind direction to avoid major loss of data. We found that the variance of the monoterpenes concentrations was a good sorting criterion. If this variance was above a threshold of 0.08 $ppbv^2$ (daytime) and 0.03 $ppbv^2$ (nighttime), concentrations and fluxes of the mentioned BVOCs were found to behave erratically and to be no more linked to climatic driving variables. These data have been rejected ending up in a limited additional 9% loss of data for the mentioned BVOCs.

This work of data preparation allowed the constitution of a thirteen months high quality database for six BVOCs and 8 months for formic and acetic acid (ongoing measurement campaign of 2011 not taken into account yet) along with the main meteorological variables (radiation, air and soil temperatures, soil moisture, precipitation, …). An overview of concentration and fluxes is given in Figure 24. In summary, filtering steps are (i) removal of background measurements, calibration and maintenance events (ii) removal of factory effects, (iii) removal of nighttime data with low-turbulence (a well-known and unavoidable limitation of the eddy-covariance method). Applying these tests reduced the data coverage from 83% to 69%, 60%, and 49%, respectively, for the most affected compounds.

We therefore end with a flux dataset constituted of more than 7000 half-hours per compound allowing robust statistical analysis (2011 campaign not included). This database encompasses all the meteorological and phenological situations met during these thirteen months at Vielsalm (night-day, hot-cold, sunny-cloudy, wet-dry, full vegetation-senescence, …) with the exception of the winter when the fluxes are expected to be very low.

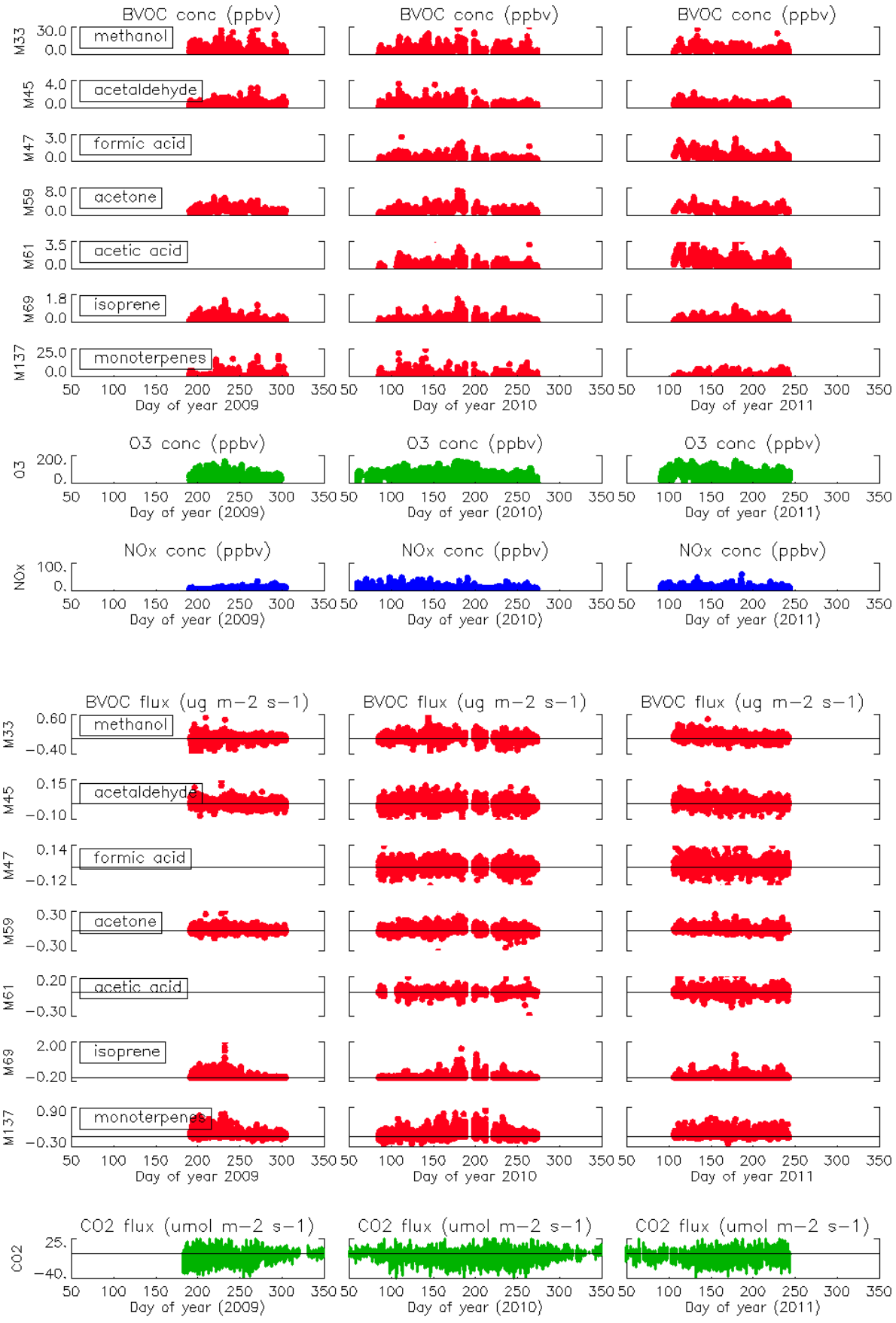


Figure 24: Overview of the filtered dataset of BVOC fluxes obtained at Vielsalm in 2009, 2010 and 2011. All concentrations are given in ppbv and all fluxes are given in μg m^{-2} s^{-1}. CO_2 fluxes are given in μmol m^{-2} s^{-1} (in green).

In parallel to BVOC flux acquisition with the PTR-MS, an eddy-covariance system was measuring CO_2, H_2O and sensible heat fluxes at the same location with even higher data coverage than the BVOC system, allowing the investigation of the relationship between BVOC emissions and the physiological fluxes (photosynthesis, respiration, transpiration).

Improvements of the flux supporting measurement set-up were implemented in 2010. The phenology follow-up was made using (i) a phenology webcam installed in March 2010 and taking pictures of the canopy every day since that date, (ii) 24 automatic below canopy radiation sensors allowing the computation of the Vegetation Area Index, (iii) about ten sampling days of manual hemispherical photography allowing the computation of Leaf Area Index and gap fraction of the canopy (performed by Partner 1). In addition, extensive measurements linked to the water cycle (sap flow, soil moisture, throughfall, …) that will be useful for the BVOC flux analysis were made by a team from UCL through another project.

Moreover, a vertical profile of five points for BVOCs and O_3 concentration measurements has been installed along the tower in June 2010. Some modifications of the calibration/multiplexer unit of the PTR-MS had to be carried out to allow simultaneous O_3 concentration measurements. Preliminary test have been performed in 2010 to scan automatically this profile with the PTR-MS alternatively with the sampling of the turbulent signal at the top of the tower. These profile concentration measurements have been carried out routinely in 2011. This profile will be of high utility for flux interpretation.

Finally in March 2011 a second eddy covariance set-up was installed in the trunk space in the near vicinity of the tower (measurement height 3.1 m). EC trunk space flux measurements will be of great interest for a better interpretation of deposition fluxes, which were for example regularly observed for methanol and acetone during the 2009 and 2010 measurement campaigns and for the estimation of soil contribution to the total flux observed above the canopy.

4.4 Data analysis

Data analysis is ongoing since the 2011 measurement campaign has not ended yet. Up to now, we have mainly investigated the isoprene/monoterpenes fluxes and the methanol fluxes. A peer-reviewed paper on this isoprene/monoterpene flux analysis has been published in “Atmospheric Environment” (Laffineur et al., 2011). For oxygenated BVOCs (methanol, acetone, acetaldehyde), two Master Thesis have been done (Hoffelt, 2010 and Gregoire, 2011) and in the specific case of methanol, a peer-reviewed paper has been accepted under minor revision in “Atmospheric Chemistry and Physics” (Laffineur et al., subm.). In the continuity of this paper,

partners 3 and 4 are now involved in a synthesis effort on methanol fluxes from terrestrial vegetation lead by the Institut für Ökologie of the University of Innsbruck. Finally, Vielsalm methanol concentrations measurements have also been used by Stavrakou et al. (2011, including Partner 3 and 4). They propose a validation at the global scale of methanol emission/deposition algorithms using a bunch of methanol concentration measurements, mainly space-based but also aircraft and surface based. The main results obtained so far by Partners 3 and 4 using the Vielsalm BVOC dataset are described below.

Generality on BVOC emissions

During the two measurement campaigns, the most important fluxes measured at Vielsalm are the monoterpenoids (m/z 137) flux and the isoprene (m/z 69) flux. Both of these fluxes are positive which indicates that the flux was always oriented from the surface towards the atmosphere, and presented a diurnal cycle. At night, isoprene fluxes were close to zero, whereas monoterpene fluxes remained slightly positive. The methanol (m/z 33) flux is also important (third place) at Vielsalm but exhibits a complex emission/deposition behavior also observed for acetaldehyde (m/z 45) and acetone (m/z 59). On the other hand, formic and acetic acid as well as MVK+MACR were characterized by very low fluxes, usually below the 3sigma flux uncertainty, and showing little response to meteorological variables. Figure shows the average of positive and negative fluxes for each BVOC compound measured during the measurement campaign of 2010.

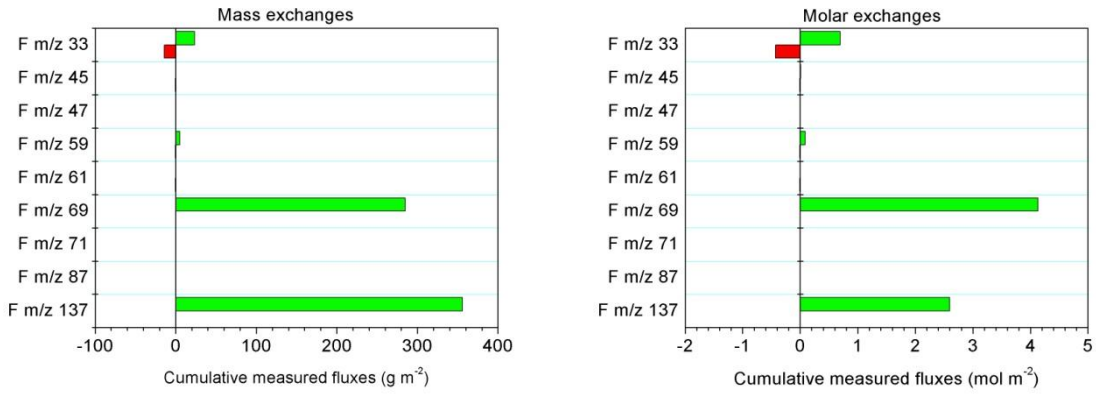


Figure 35: Cumulative measured emissions (green) and absorptions (red) of each VOC in terms of mass (left) and molar (right) quantities at Vielsalm for the period May-September 2010.

Sources of BVOC emissions

The Vielsalm forest is heterogeneous in terms of species. The zone that influences the measured flux is planted with *Pseudotsuga menziesii*, *Fagus sylvatica* and *Picea abies*/*Abies alba*. One main difficulty when measuring fluxes above such a heterogeneous ecosystem is to determine which sources are responsible for the

measured flux. The footprint climatology suggested that, during the observation period, the fluxes originated mainly from the south-west, a zone covered predominantly by *Fagus sylvatica* and *Picea abies*/*Abies alba,* and to a lesser extent from the north-east, where *Pseudotsuga menziesii* predominated. Footprint analysis suggested that the flux measured by the eddy covariance system never came from a unique source, but more often from a mixture of species. Under these conditions, it was difficult to characterize univocally the emission characteristics of each emitting species. By combining the footprint analysis with the land use map (Figure), we found that monoterpene flux increased linearly with the *Fagus sylvatica* flux contribution when it exceeded 40%. This suggests that *Fagus sylvatica* emits more monoterpenes than the other species of the ecosystem, which accords with previous studies (Holzke et al., 2006; Moukhtar et al., 2005). Other species could also contribute to the emissions of monoterpenes, such as *Abies alba* (Moukhtar et al., 2006) or *Picea abies* (Filella et al., 2007). However, Moukhtar (2006) showed that *Fagus sylvatica* should emit at least 10 times more than *Picea abies* or *Abies alba*, which accords with our footprint analysis.

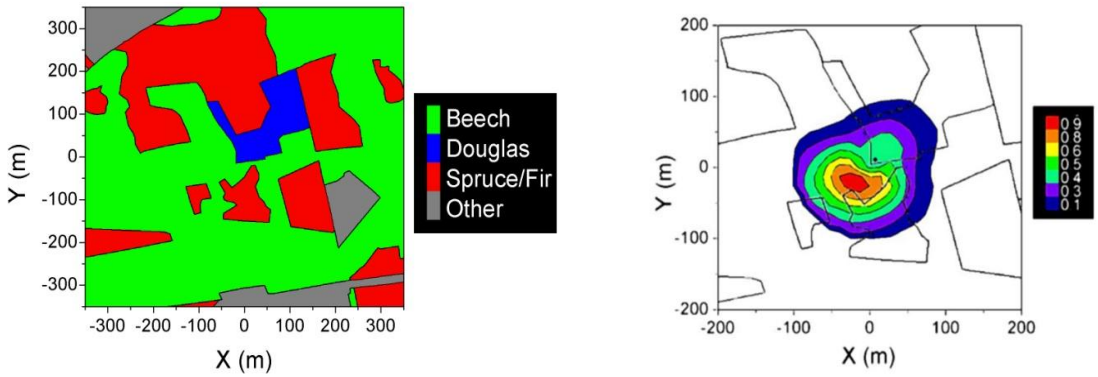


Figure 36: *Left*: Land-use map around the tower. *Right*: Normalised and cumulated day footprint from July to September 2009 superimposed on the vegetation map. Tower location: (0,0) , North direction: (0,Y).

The analysis also showed that the isoprene flux decreased linearly with the *Fagus sylvatica* flux contribution when it exceeded 40%, suggesting that this beech is not an isoprene source. Moukhtar et al. (2006) also found that *Abies alba* was not an isoprene source, but Filella et al. (2007) showed that *Picea abies* could be one. This would suggest that *Picea abies* was the sole species on the site emitting isoprene. This is not incompatible with our results, but cannot be validated by the footprint analysis because the contribution of this species to the measured flux never exceeded 40%.

Isoprene/monoterpenes

During the day, isoprene and monoterpene fluxes were mainly controlled by the air temperature and the light. The seasonal evolution of the isoprene/monoterpene emissions was studied using a monthly temperature (C_T) and light (C_L) dependence function deduced from our results to standardize the fluxes. A seasonal decrease in the standard emission factors was observed (Figure). The standard emission factor (30°C, 1000 µmol m^{-2} s^{-1}) fell from 0.91 ± 0.01 to 0.56 ± 0.02 µg m^{-2} s^{-1} and from 0.74 ± 0.03 to 0.27 ± 0.03 µg m^{-2} s^{-1} for isoprene and monoterpene fluxes respectively.

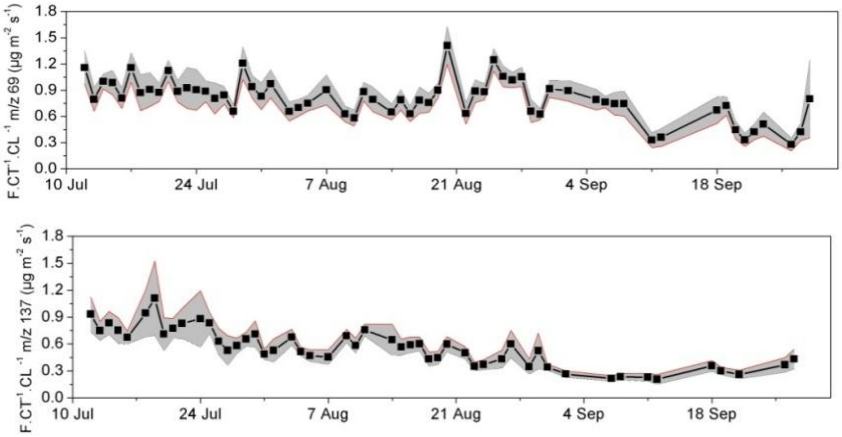


Figure 37: Mean diurnal evolution (PPFD > 300 µmol m^{-2} s^{-1}) of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized for temperature (30°C) and PPFD (1000 µmol m^{-2} s^{-1}). The grey area represents the 95% confidence intervals.

BVOC flux temperature dependency is characteristic of an enzymatic reaction and could therefore characterize the isoprene or monoterpene synthases as well as the enzymatic reactions of the isoprene/monoterpenes biosynthetic pathway.
BVOC flux light dependency would be a direct consequence of the strong link between the gross primary production (GPP, also determined by eddy-covariance) and isoprene/monoterpene emissions (Figure) because the isoprene/monoterpene precursor is a sub-product of photosynthesis. The linear relationship observed in July would suggest that the isoprene/monoterpene precursor (via GPP) was the main limiting factor in BVOC synthesis. The slope of the BVOC/GPP relationship depends on enzymatic activity. It is therefore likely that the decrease in this slope during the season corresponded to a decrease in this activity. This seasonal decrease could be due to a leaf acclimation to temperature and radiation that could affect enzymatic activity over the long term. For *Fagus sylvatica*, leaf senescence could also have contributed to the decrease in monoterpene synthase activity. The non-linearity of the BVOC emissions to GPP responses in September and the appearance of saturation at a large GPP clearly indicate that other factors start to limit the BVOC synthesis at that time of the year. The limitation appears to be more critical for monoterpenes than for isoprene and could be due to saturation in the substrate of the enzyme activity through the biosynthetic pathway and/or saturation in the

substrate of the monoterpene synthase activity and (to a lesser extent) of the isoprene synthase activity during the season. To our knowledge, it is the first time that the seasonal evolution of the isoprene/monoterpene synthesis efficiency is shown at the ecosystem scale.

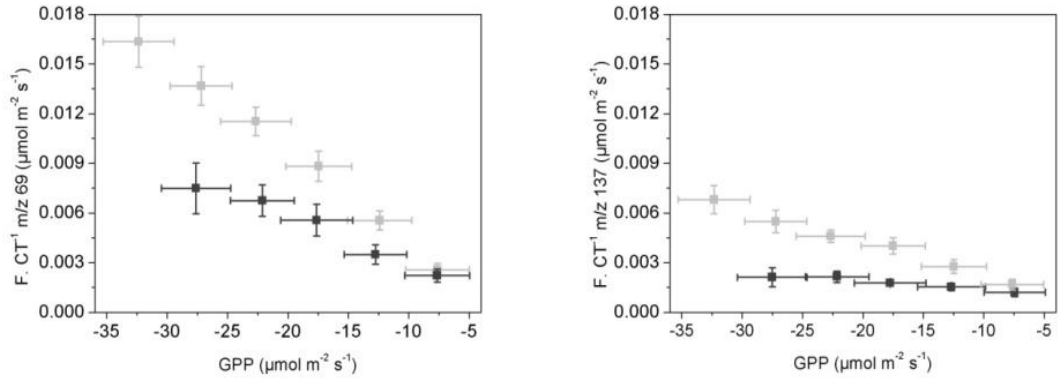


Figure 38: Bin averages of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized at 30°C (n≥14, error bars are 95% confidence intervals) in relation to the gross primary production (GPP) for July 2009 (light grey) and September 2009 (dark grey).

During the night, a slight positive flux of monoterpenes was observed that seemed to be driven by air temperature. The standard emission factor (30°C) for night-time monoterpene fluxes was equal to 0.093 ± 0.019 µg $m^{-2}s^{-1}$. There could be several reasons for this night-time monoterpene flux. First, it could result from de-storage. Unlike isoprene, some of the monoterpene production can be stored in plant tissues (especially coniferous species) from which it can diffuse progressively to the atmosphere where it is volatilized. A second reason for monoterpene night-time fluxes could be soil production through various mechanisms. Litter decomposition has the potential to contribute significantly to these fluxes, especially fresh litter. An emission from the storage pools of the roots with a mechanism similar to tissues storage emissions can also contribute to monoterpene emissions, as well as the activity of specific micro-organisms. In summary, it is likely that night-time monoterpene fluxes resulted from both de-storage in the conifers and soil emission. However, the results of the literature survey suggest that de-storage fluxes would be at least one order of magnitude larger than those of soil emission.

Methanol

Methanol is the most significant BVOC in the atmosphere. It influences the OH concentration in the troposphere, the tropospheric ozone production and the formaldehyde production. In this context, the comprehension of methanol emission/deposition mechanisms is important especially from long-term measurements. At Vielsalm, the methanol fluxes were bi-directional, generally negative (deposition) during the night and generally positive during the day. During the summer-autumn period, the night depositions were more important than the day

emissions, the inverse situation was observed during the spring period. The methanol deposition increased linearly with friction velocity and with atmospheric methanol concentration. The humidity seemed to be also an important driving variable, the depositions being more important when the atmospheric water vapor pressure was close to saturation (Figure). In these humid conditions, water films are initiated and favored on the vegetation surface. The methanol being very soluble in water, the deposition of methanol is enhanced by the presence of these water films.

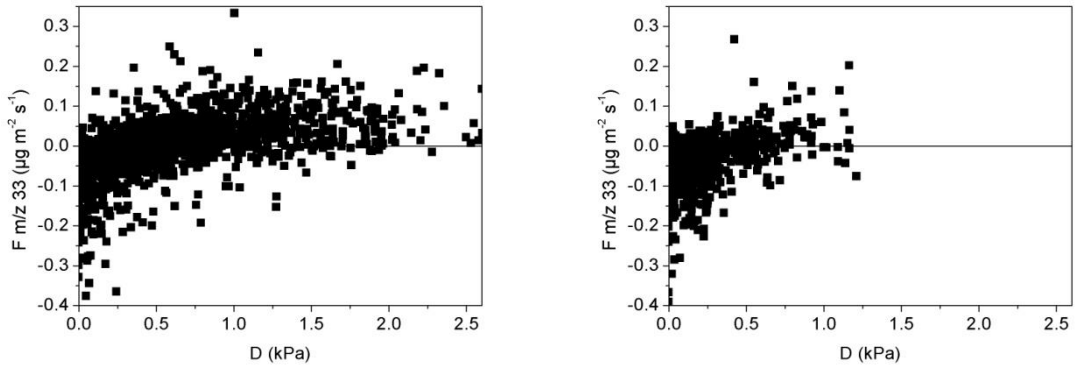


Figure 39: Methanol flux (m/z 33) in relation with the water vapor pressure deficit (D) during the day (left) and during the night (right) in 2009.

In order to quantify the non-biogenic methanol exchanges, we developed a model of absorption/desorption, based on the two-layer model of Liss and Slater (1974) and the model developed by Sutton (1998) to explore the ammonia adsorption/desorption effect. It took atmospheric methanol concentration, friction velocity, water vapor pressure deficit, precipitations and Henry's law constant depending on temperature into account. The model was calibrated on night deposition fluxes measured during the summer-autumn of 2009 and validated on 2010 data. Simulation reproduced well measurements during most of the measurement period (Figure), as well in summer-autumn 2009, as during summer 2010. This suggests that, most of the time, the measured fluxes (night and day) can be mainly explained by a physical absorption/desorption process. At the end of October 2009, we overestimated the deposition because our model does not include the decreasing of leaves surface.

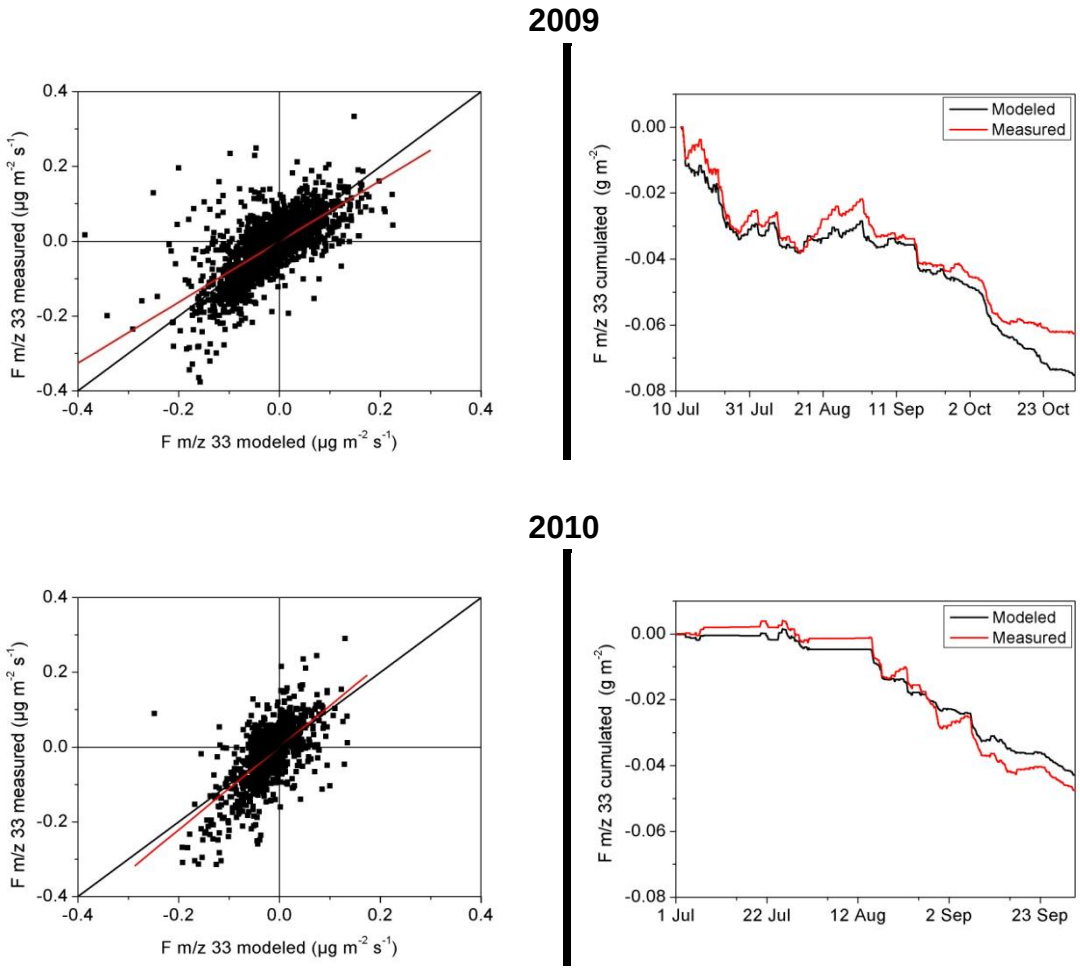


Figure 40: *Left*: comparison between the measured and modeled methanol (m/z 33) fluxes for 2009 ($a = -3.6\ E^{-4} \pm 0.0012$; $b = 0.81 \pm 0.02$; $R^2 = 0.47$) and 2010 ($a = -6.5\ E^{-5} \pm 0.002$; $b = 1.10 \pm 0.04$; $R^2 = 0.43$). *Right*: cumulative measured and modeled methanol fluxes.

In contrast, during one 2010 spring week, significant differences appeared between simulations and measurements (Figure), suggesting the pre-eminence of biogenic fluxes at that time. They appeared during a period presenting a co-occurrence of sunny conditions and important leaf development. These biogenic emissions corresponded probably to the demethylation of pectin in the primary cell walls and were mainly controlled by the air temperature.

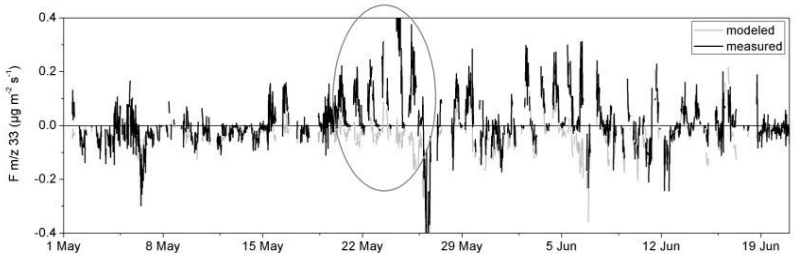


Figure 41: Representation of measured and modelled fluxes of methanol (m/z 33) during May-June 2010 period.

Using this model, we are able to disentangle emissions and depositions and propose a standard emission factor, describe its seasonal evolution, propose light and temperature dependencies for the emissions and investigate more deeply the depositions which play an important role at Vielsalm, These information are crucial for the improvement of the methanol exchange algorithms, depositions having been shown recently to be underestimated for oxygenated BVOCs (Karl et al., 2010).

WP5 Integration

5.1 Growth room and forest abiotic (temperature) and biotic (aphid) stress

We provide a study comparing BVOC emissions of *Fagus sylvatica* L. in controlled and natural environmental conditions. A young and adult beech trees were exposed to short-term temperature variations in growth room conditions and in a semi-urban experimental forest, respectively. This study attempts to clarify how short-term temperature variation between days influenced the ratio between MT emissions and Pn. Within a temperature range of 17-27°C and 13-23°C in the growth room and forest, respectively, representing a typical variation on a summer day in Belgium forests, the MT/Pn carbon (C) ratio increased 10-30 fold, for both the growth room and forest, respectively. The observed ratios were rather small when compared to the ratios found in literature for other deciduous and even some coniferous tree species, ranging between 0.01-13% under normal conditions. An exponential increasing trend between MT/Pn C ratio and air temperature was observed in both conditions. Beech trees re-emitted a low fraction of the assimilated C back into the atmosphere as MT. This fraction increased from 0.01-0.12% and 0.01-0.30% with a temperature rise from 17-27°C and 13-23°C in growth room and forest conditions, respectively. These results might have important consequences for global climate change research, since the described mechanism could act as a positive feedback loop in case of expected increasing temperatures.

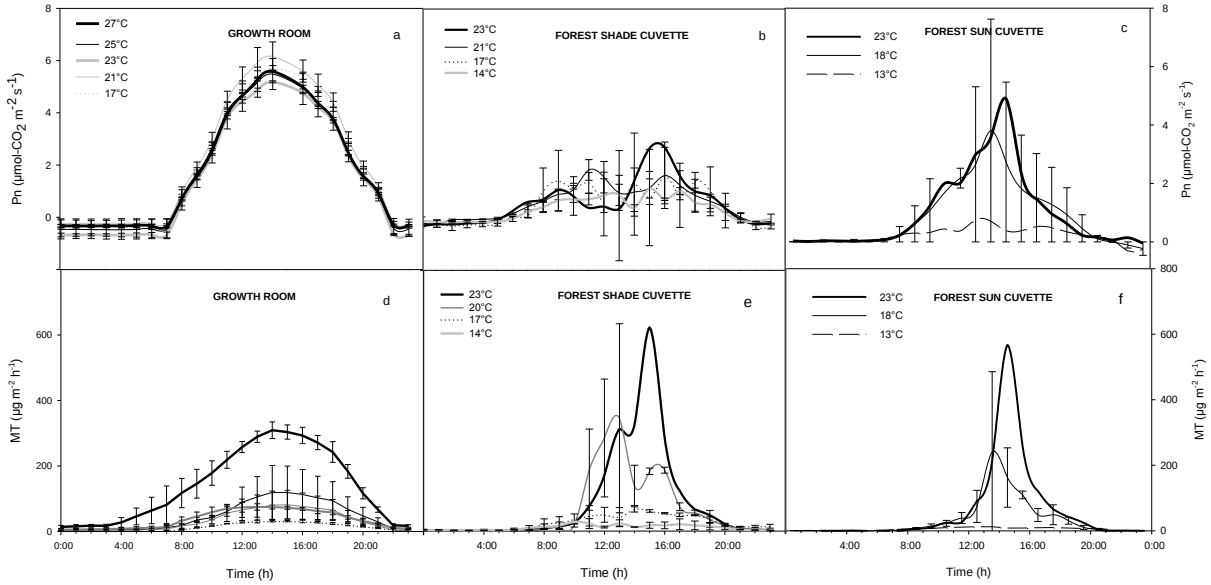


Figure 42: (a-c) Mean diurnal patterns of net photosynthesis (Pn) for each imposed temperature. Negative values represent the night-time dark respiration. (d-f) Mean diurnal patterns of monoterpenoids for each imposed temperature. Low night-time emissions were observed in growth room experiments only.

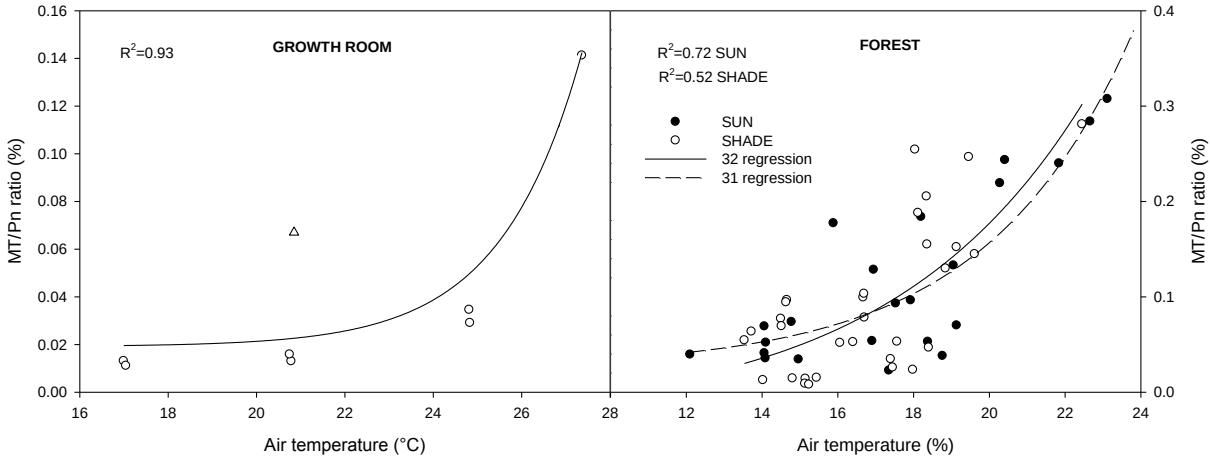


Figure 43: Exponential increasing trend of MT/Pn C ratio as a function of air temperature observed in growth room (a) and forest (b) experiments.

The triangle in Figure represents the day after temperature was changed from 27 to 21°C. The beech leaves needed a 1-day adaptation time and showed a higher calculated ratio compared to other days of 21°C. Therefore, this day was considered as an outlier, and was not included in the calculation of the mean value. A peer-reviewed paper on these experimental results is published in Atmospheric Environment (Šimpraga et al. Comparing monoterpenoid emissions and net photosynthesis of beech (*Fagus sylvatica* L.) in controlled and natural conditions).

Aelmoeseneie forest canopy experiment

The results of the canopy experiment in the forest Aelmoeseneie were split into (1) long-term (entire measurement campaign) and (2) short-term (diurnal patterns) results. From the emitted BVOC compounds, monoterpenes (there was no detection of oxygenated compounds eg. linalool during the canopy experiment) were studied in detail.
Online recording of net photosynthesis (CO_2 exchange), Photosynthetic Active Radiation (PAR) and leaf temperature were performed simultaneously with Proton Transfer Reaction Mass Spectrometry (PTR-MS) measurements of monoterpene emission for the selected cuvettes on the third platform (at 22 and 26 meter height). Out of these measurements, we concluded that measurements of the first three variables could not account for the observed differences in monoterpene emissions between both cuvettes (Figure) (Moukhtar et al., 2005, Dindorf et al., 2006).

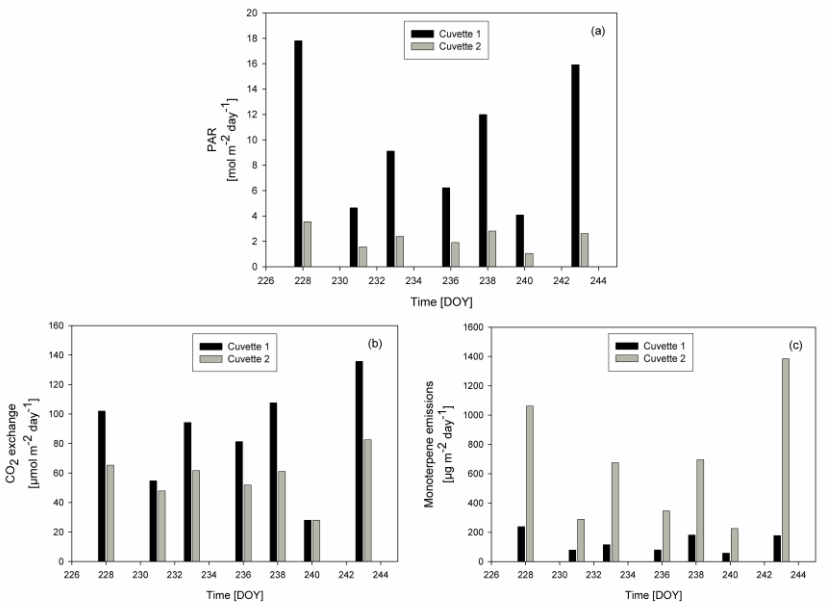


Figure 44: Seven selected days indicating photosynthetic active radiation (a), photosynthesis (b) and monoterpene emissions (c) of an enclosed branch of European beech during the field experiment in August-September 2008. Monoterpene emissions and photosynthetic levels are represented as hourly averages. DOY represents the day of the year.

An example of a sunny day (30/08/08) is presented in Figure . On this day, leaves from the branch enclosed in cuvette 2 (lower cuvette on platform 3) assimilated less CO_2 (Pn max = 5 µmol m^{-2} s^{-1}) in comparison with the leaves in cuvette 1 (Pn max = 6 µmol m^{-2} s^{-1}). In general one can say that the sunny day measurements and all prevailing conditions (higher temperature, higher PAR and higher Pn) are more advantageous for cuvette 1 in order to synthesise higher amounts of monoterpenes and emit them into the atmosphere. On the contrary, monoterpene emissions were remarkably higher for the leaves in cuvette 2 (MT = 650 µg m^{-2} h^{-1}) in comparison with the leaves in cuvette 1 (MT = 50 µg m^{-2} h^{-1}).

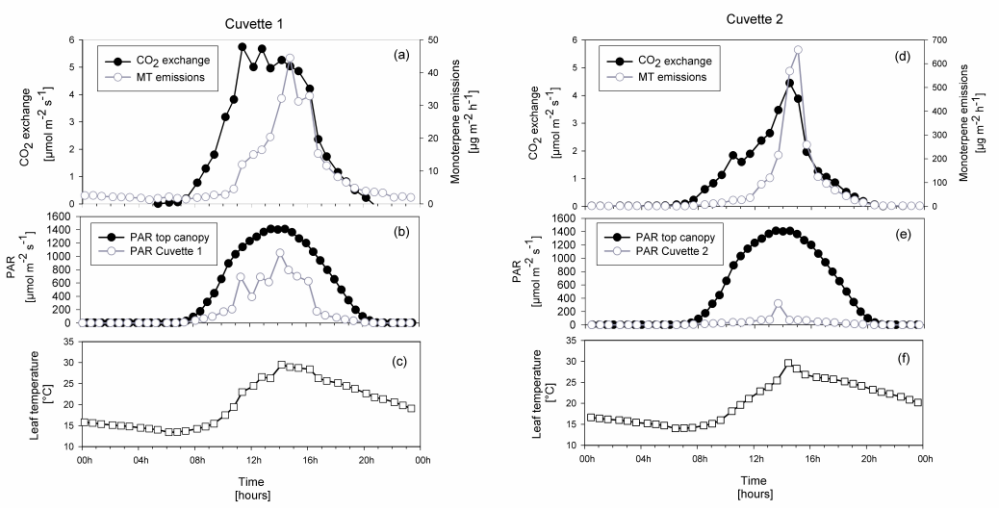


Figure 45: (a) Diurnal patterns of net photosynthesis and total monoterpene emission for cuvette 1; (b) Photosynthetic active radiation (PAR) on top canopy and in cuvette 1; (c) Leaf temperature for cuvette 1; (d) Diurnal patterns of net photosynthesis and total monoterpenoid emission for cuvette 2; (e) Photosynthetic active radiation (PAR) on top canopy and in cuvette 2; (f) Leaf temperature for cuvette 2. Negative values represent night-time dark respiration. All data are measured on 30/08/2008.

Using offline measurements we found that a different leaf type was present in the two cuvettes: sun adapted and shade adapted leaves. Both leaf types have different physiological characteristics and were exposed to different radiation and temperature regimes during the measurement campaign. Especially the difference in light regime was distinct and a pronounced sunfleck pattern was observed for sunny days for the shade adapted leaves in the lower cuvette (Figure). The differences in physiological characteristics of the leaf types were followed up with measurements of Specific Leaf Area (SLA), leaf thickness, leaf chlorophyll content (CCI, data not shown) and leaf pigment content of the sun and shade adapted leaves. It can be observed that the Specific Leaf Area (SLA) and calculated leaf thickness showed a clear difference between sun and shade adapted leaves. Similar results were already stated in earlier published articles (Sarijeva et al., 2007).

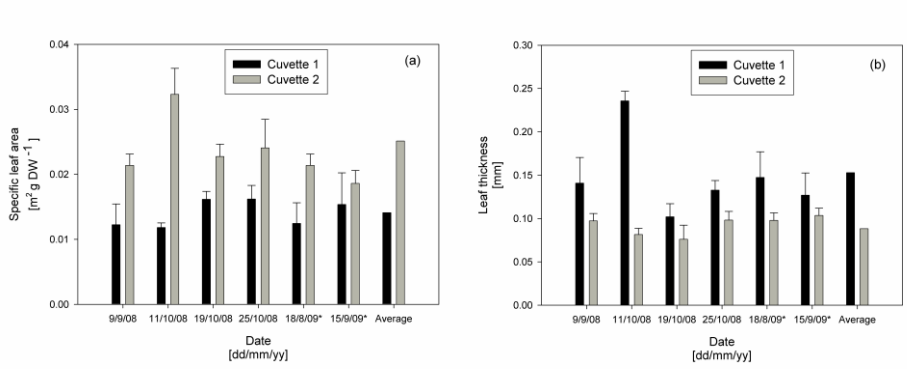


Figure 46: Measured specific leaf area and calculated leaf thickness indicating a clear difference of sun and shade leaves.

These results stress the importance of the physiological status of the leaves in future research of BVOC emissions. Existing emission algorithms, such as the Guenther 97 algorithm do not take in account that leaf physiology can play an important role in differences in VOC emissions patterns. We thereby suggest that an incorporation of a new “physiology” parameter in new algorithms can result in a better understanding of emission patterns and will results in less systematic under or overestimation of existing emissions.

5.2 Improvement of emission algorithms

Analysis of the BVOC emissions observed in the 2008 canopy experiment and evaluation of improved emission algorithms

Seasonal BVOC emission responses

Daily standard emission factors (SEF) as defined in the light and temperature dependent algorithm of Guenther et al. (2007) (hereafter referred to as G97) have been calculated for the enclosed sunlit and semi-shaded branches which were accessible from the third platform of the measuring tower. These SEF values correspond to the slope of the linear fit through the data points representing the experimental monoterpene emission rates as a function of the product C_T x C_L, with C_T and C_L being the temperature and light response functions in G97, respectively. The temporal variation of the SEF during the campaign is shown in Figure for the sunlit leaves (cuvette 3.1 @ 25 m) and for the semi-shaded leaves (cuvette 3.2 @ 24 m). Also shown on this figure are some recent literature data from *Fagus sylvatica* L. trees.

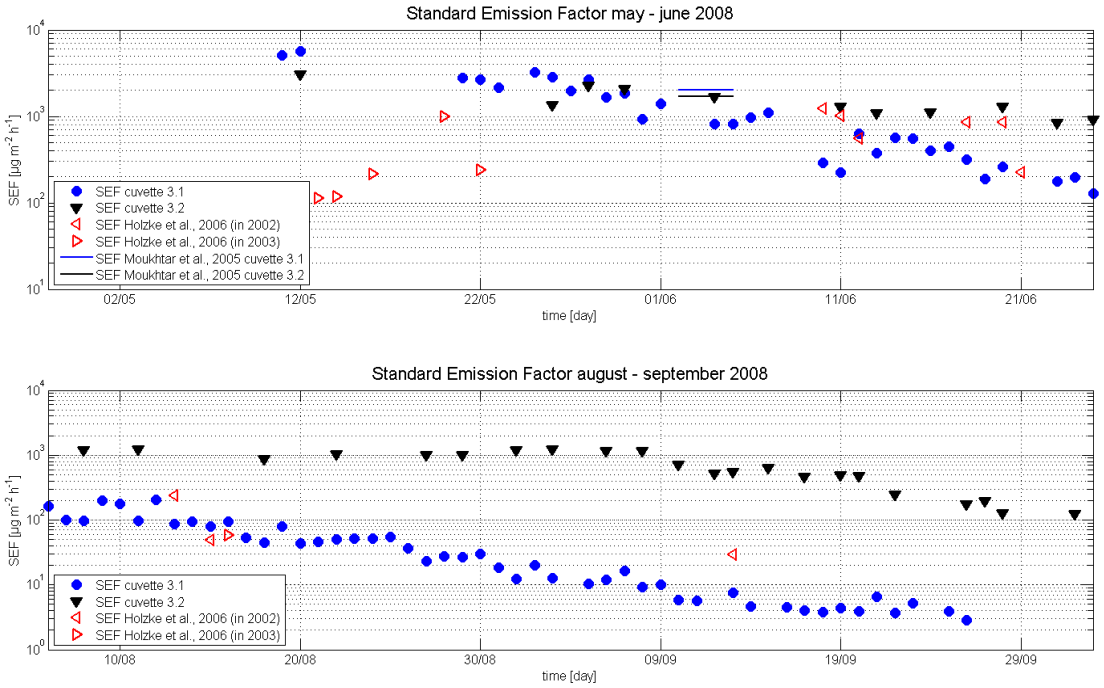


Figure 47: Seasonal variation of the standard emission factor (SEF) for beech leaves in cuvette 3.1 and cuvette 3.2 on the third platform of the experimental tower in the forest Aelmoeseneie.

From this figure it is clear that the G97 SEF exhibits a strong seasonal variation. Whereas the SEF of the sunlit branch strongly decreased over the entire measurement period, the one of the semi-shaded branch in the upper canopy showed a more constant behavior until the beginning of September. The upper canopy SEF values are in fair agreement with values reported by Moukhtar et al. (2005) and Holzke et al. (2006) for mature leaves of *Fagus sylvatica* L. trees in a natural environment. In order to enable comparison, the values from Moukhtar et al. (2005) in early June were multiplied by the experimentally determined specific leaf area (SLA) value for sunlit leaves in mid-August. However, SEF values obtained for newly developed leaves in the present study were found to be more than an order of magnitude higher than the ones reported by Holzke et al. (2006) for the same period.

In summary, the canopy experiments have shown that SEF values for *Fagus Sylvatica* L. exhibit a strong seasonal dependence, as well as a strong dependence on the position of the leaves in the canopy, which is probably related to differences in physiological status of the leaves.

Evaluation and adjustment of emission algorithms against the observed monoterpene flux dataset

Evaluation and/or adjustment of existing emission algorithms was performed against different subsets of the acquired monoterpene emission rate dataset obtained during the growth season of 2008. The first subset (early May) consists of three days from

the first part of May which are characterized by strong leaf growth and consequently large methanol emissions (up to 500 µg m^{-2} h^{-1}). The second subset (May-June) refers to a period where leaves have reached mature dimensions. Data from the third subset (June) were obtained in a period during which the sunlit branch was infested by aphids (*Phyllaphis Fagi* L.). Finally, data from August and September constitute the fourth subset.
In Figure, averages over the different subsets of the measured and modelled diurnal hourly-averaged monoterpene emission rates are shown.

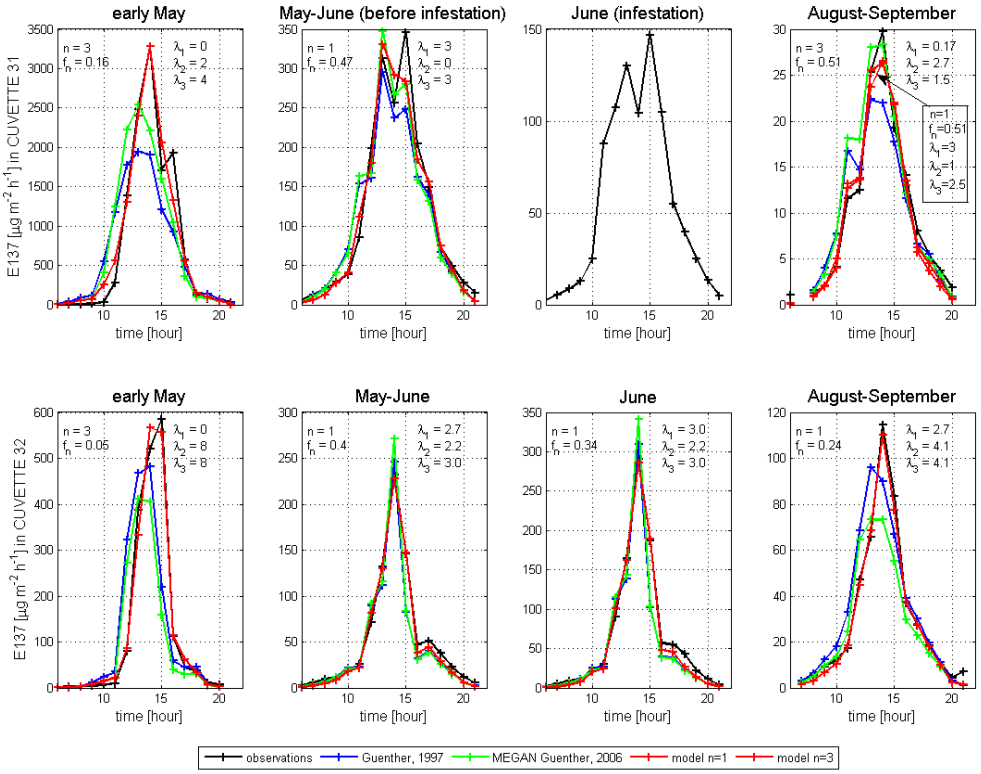


Figure 48: Averaged diurnal monoterpene emission rate for sunlit (cuvette 3.1) and semi-shaded (cuvette 3.2) beech leaves and comparison with different algorithms.

A clear discrepancy can be noticed between the observations (in black) and the emission rates calculated with the G97 (in blue) and G06 (MEGAN, in green) algorithms, especially in early May and August-September. Both algorithms overestimate the emissions in the morning, and underestimate the emissions in the afternoon. The observed behaviour is therefore qualitatively similar to the apparent hysteresis of emissions observed in the growth chamber experiment under controlled conditions (2007).

In order to obtain a better agreement with the experimental data, several parameters appearing in the MEGAN G06 algorithm (Guenther et al. 2006) were optimized by

minimizing the overall bias between the model and the data, i.e. the cost function f, given by:

$$f = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{m_i}\frac{\left(E_{ij}^{\mathrm{mod}} - E_{ij}^{obs}\right)^2}{\left(\sigma\left(E_{ij}^{obs}\right)\right)^2 + C^2} \qquad (1)$$

with N the number of days in the data set, m_i the number of observations per day, E_{ij}^{obs} the observed emission flux averaged over the 18 minutes measuring interval, $\sigma(E_{ij}^{obs})$ the corresponding standard deviation and E_{ij}^{mod} the averaged modeled emission flux, defined as:

$$E_{ij}^{\mathrm{mod}} = \varphi_i \cdot \gamma_{T,ij} \cdot \gamma_{P,ij} \qquad (2)$$

with φ_i a fitted SEF value for each day (for which the SEF factor derived by fitting the G97 algorithm to the experimentally determined emission rates for the corresponding day was used as a first guess), and γ_T and γ_P the temperature and light response function, respectively. The latter are given by the following equations:

$$\gamma_T = \gamma_{T,G97} \cdot e^{0.1\left[T_{10d}-297\right]} \cdot e^{\lambda_1 \cdot 0.05\left[T_{nh}-297\right]} \qquad (3)$$

$$\gamma_P = C_{L,G06} \cdot \frac{\left(\lambda_3 \cdot \alpha\right) \cdot P}{\sqrt{1+\left(\lambda_3 \cdot \alpha\right)^2 \cdot P^2}} \qquad (4)$$

in which α and $C_{L,G06}$ are given by:

$$\alpha = 0.004 - 0.0005 \cdot \ln\left(P_{10d}\right) \qquad (5)$$

$$C_{L,G06} = 0.0468 \cdot \exp\left(\lambda_2 \cdot 0.0005 \cdot \left(P_{nh} - P_0\right)\right) P_{10d}^{0.6} \qquad (6)$$

In the above formulas, T [K] and P[µmol $m^{-2}s^{-1}$] are the instantaneous leaf temperature and PPFD and T_{nh} [K], P_{nh} [µmol $m^{-2}s^{-1}$],T_{10d} [K], P_{10d} [µmol $m^{-2}s^{-1}$] are the averaged temperature and PPFD values over the past *n* hours or 10 days. P_0 is equal to 200 µmol $m^{-2}s^{-1}$ for sunlit leaves and 50 µmol $m^{-2}s^{-1}$ for shaded leaves. The parameters λ_1 and λ_2 respectively determine the impact of the previous PPFD and temperature conditions experienced by the leaves, i.e. light and temperature history, on the instantaneous emissions. The λ_3 parameter strongly influences the shape of the light response curve, with high values indicating saturation of the emissions at low PPFD values. This parameter is expected to depend strongly on the average PPFD to which the leaves are accustomed (Harley et al., 1996) and thus on the position of the leaves in the canopy. By setting λ_1, λ_2 and λ_3 equal to 1 and n equal

to 24, γ_T and γ_P correspond to the normalized leaf temperature and light response functions of the original MEGAN algorithm.

The improvement of the fitted algorithm with respect to the original MEGAN algorithm was quantified in terms of the normalized cost function, f_n, defined as $f_{adjusted}/f_{MEGAN}$.

The modeled emissions with the fitted algorithm, along with the optimized values for n, λ_1, λ_2 and λ_3 and the normalized cost function are shown on Figure for the different subperiods. In order to better capture the higher emissions within these periods, the parameter C in equation (1) was set equal to the median of the observed emissions for each of the subsets. The fitted algorithm generally performs much better in describing the observations than the G97 and the MEGAN algorithm and the time delay of the emissions and the resulting light hysteresis are quite well taken into account. The results indicate a dependence of the emissions on the temperature and PPFD conditions of the previous 1-3 hours, much less than what was observed in the growth chamber from beech saplings (n = 10-13 hours). With the exception of the August-September period for the sunlit branch, the large values of λ_3 (3-8) indicate that saturation of the emissions generally occurs at much lower PPFD values than in the original MEGAN algorithm, in which the shape of the light response curve was optimized for isoprene emissions. Similar large values for λ_3, ranging between 1.9 and 5) were inferred for the beech saplings in the growth chamber experiments in 2007. Furthermore, the λ_3 values for the semi-shaded branch were lower than or equal to the ones for the sunlit branch, suggesting acclimatization of the leaves to the light environment with saturation at lower PPFD levels for the semi-shaded branch.
The anticorrelation of λ_1 and λ_2 for the sunlit branch with one of both parameters close to zero and with the identity of the non-zero parameter varying from subset to subset reflects the large co-variation of PPFD and temperature for this branch, as the averaged temperature and PPFD over the previous *n* hours appear as a linear combination in the emission algorithm.

Evaluation of emission algorithms at Vielsalm using a canopy environment model

The long-term dataset of stand scale BVOC flux measurements (see WP4.3) is used to evaluate different emission algorithms with the canopy environment model MOHYCAN (Wallens, 2004). This model calculates the visible and NIR radiation fluxes for shaded and sunlit leaves at 8 canopy layers, and determines the leaf temperatures. The meteorological input variables (air temperature, diffuse and direct solar radiation, wind speed and relative humidity at canopy top) are obtained from the measurements at the top of the tower. Gaps in the time series are filled based on high-resolution ECMWF analyses. The forest patch impacting the measurements

comprises both deciduous and coniferous trees, in similar proportions. The seasonal LAI profile is based on available measurements (Figure). The beech LAI values were forced to about zero in winter, noting that the measured VAI is expected to overestimate the LAI.

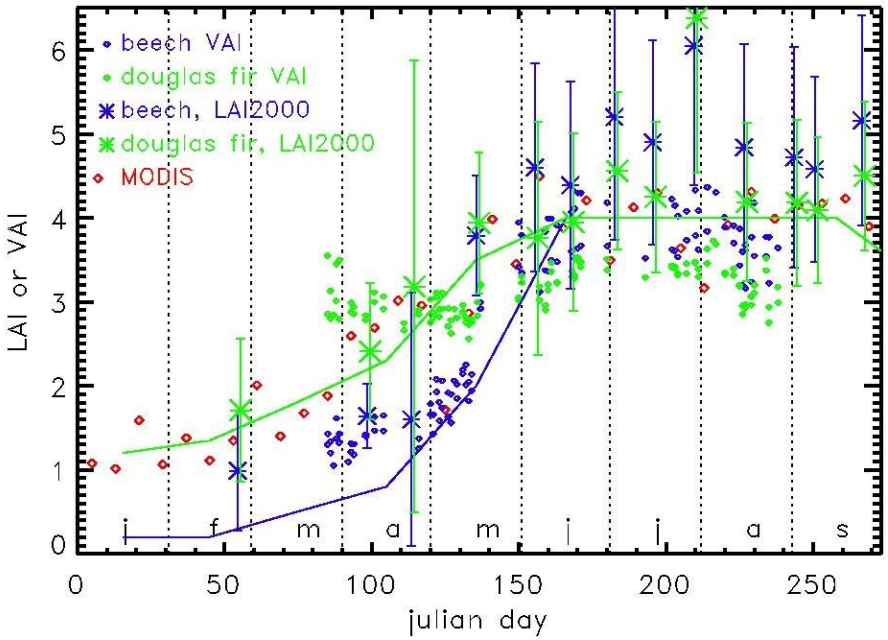


Figure 49: LAI2000 measurements (R. Soubie, pers. comm.; Soubie et al., 2010) and automatic measurements of the vegetation area index (VAI) at a beech stand (dark blue) and a Douglas fir stand (green) around the tower near Vielsalm in 2010. Also shown are the LAI data from the MODIS instrument within less than 3 km of the tower (Shabanov et al., 2007). The LAI values used in the canopy vegetation model are shown as green (for coniferous trees) and dark blue (deciduous) lines.

The emissions (µg m^{-2} s^{-1}) are calculated as $F_{\mathrm{mod}} = \varepsilon \cdot \sum_i C_{L,i} \cdot C_{T,i} \cdot \Delta \mathrm{LAI}_i$, where ε is a standard emission factor (µg m^{-2} s^{-1}), assumed to be constant as a first approximation; $C_{L,i}$ and $C_{T,i}$ are light and temperature activity factors calculated at each canopy layer i; and $\Delta \mathrm{LAI}_i$ is the LAI in that layer.

Isoprene and monoterpenes

The tested isoprene algorithms include G93 (Guenther et al., 1993), MEGAN (Guenther et al., 2006), and a modified version (G93L) of G93, with $C_{T,i} = \exp(\beta \cdot (T_i - 303))$, where T_i is leaf temperature and $\beta = 0.17\,\mathrm{K}^{-1}$ (Laffineur et al., 2010). ε is expressed per unit leaf area in G93 and G93L, and per unit soil area in MEGAN. The emissions of monoterpenes consist of a main light-dependent component, parameterized as in the isoprene algorithm G93 or MEGAN, and a smaller light-independent component parameterized as $F_{Li} = \varepsilon_{Li} \cdot \exp(\beta_{Li} \cdot (T - 303))$, with $\beta_{Li} = 0.06\,\mathrm{K}^{-1}$ and $\varepsilon_{Li} = 0.028$ µg m^{-2} s^{-1} (here per unit *leaf* area) based on night time measurements in 2009 (Laffineur et al., 2010).

As seen on Figure and Figure , both the diurnal cycle and the day-to-day variability of the emissions are well reproduced by the model. The Pearson's correlation coefficients between modelled and observed fluxes are ~0.88 for isoprene and ~0.73 for monoterpenes in 2009, with only minor (~0.01) differences between the different algorithms. Nevertheless, MEGAN leads to overestimated isoprene emissions in the late afternoon, a feature also noted in 2010 (not shown).

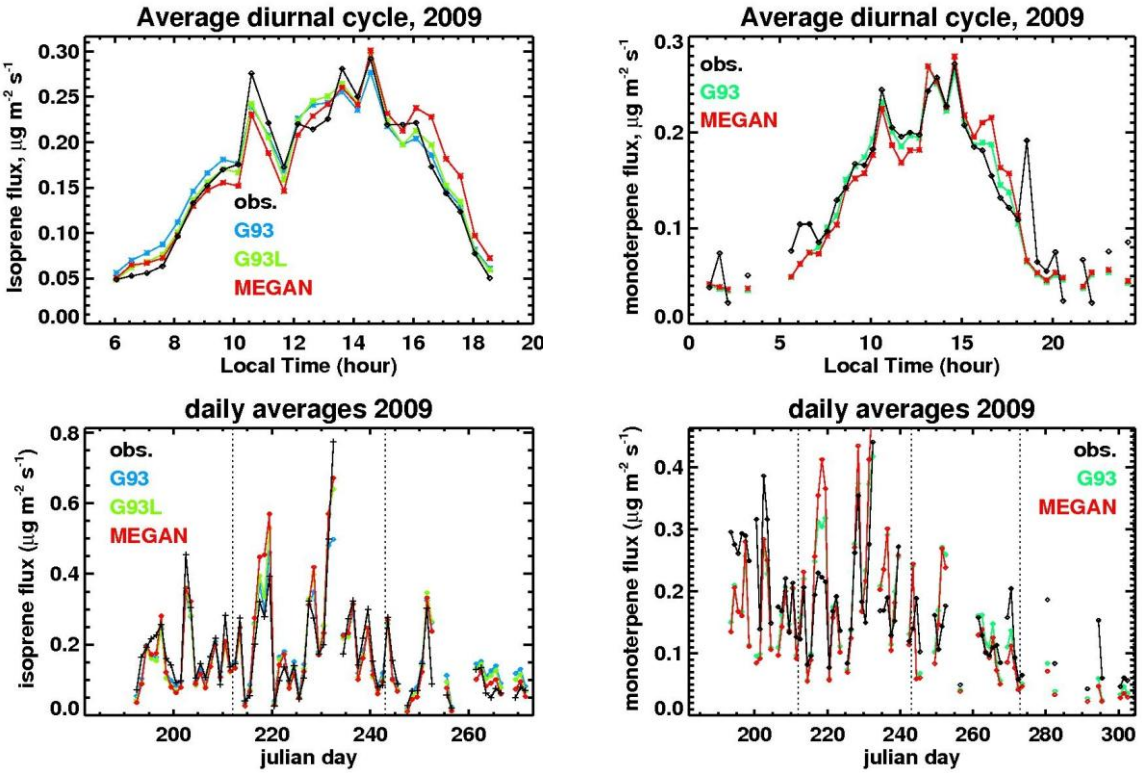


Figure 50: Average diurnal cycle of observed and modelled emissions in July-September 2009 (top); daily averaged observed and modelled emissions (bottom).

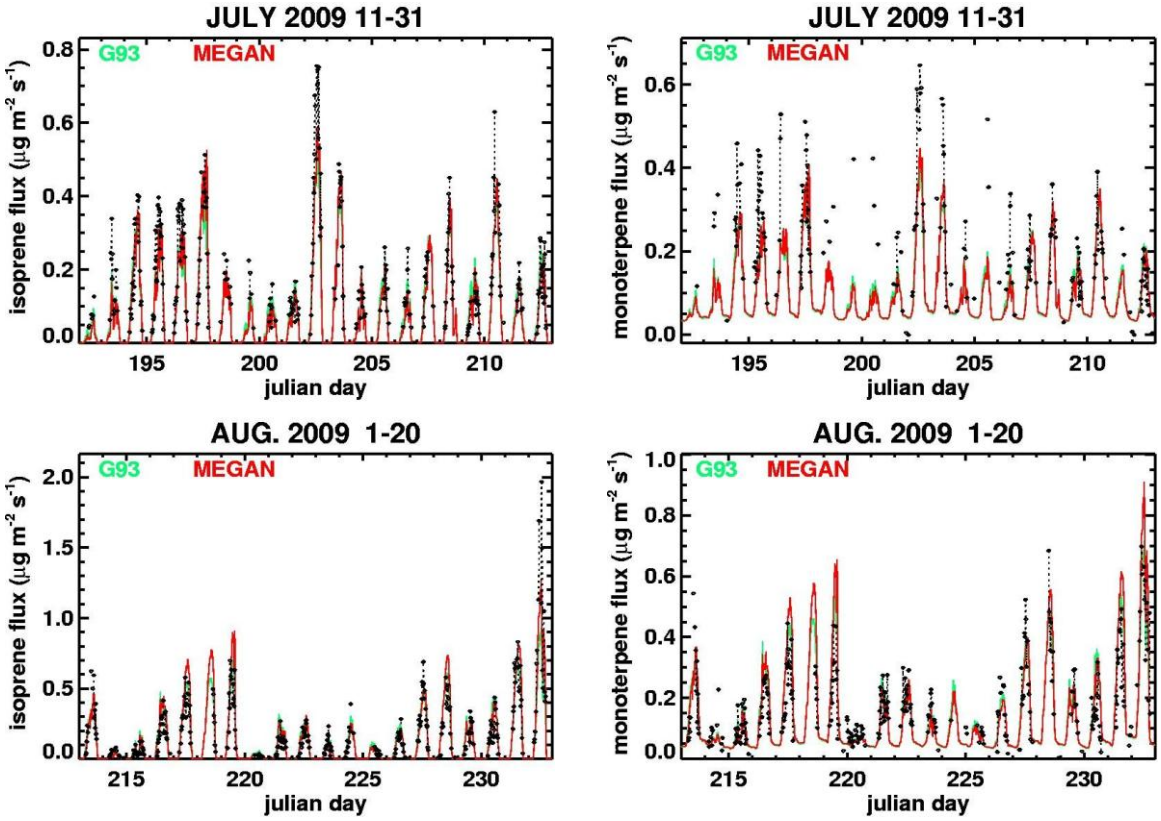


Figure 51: Observed and modeled isoprene (left) and monoterpenes (right) fluxes in July/August 2009.

In the calculations above, the standard emission factor (SEF) was held constant throughout the measurement period. Monthly SEF values can be determined using $\varepsilon = {< F_{obs} >}/{< F_{mod}(\varepsilon = 1) >}$, where <> denotes monthly averages, whereas F_{obs} and F_{mod} denote the observed and modelled fluxes. On Figure , the isoprene SEF is seen to maximize in July-August. The temporal variation of the SEF is well described by the leaf age activity factor (γ_{age}) of the MEGAN algorithm, parameterized from the seasonal LAI profile (Guenther et al., 2006). For monoterpenes, the SEF is seen to monotonically decrease between April and September, in consistence with previous studies.

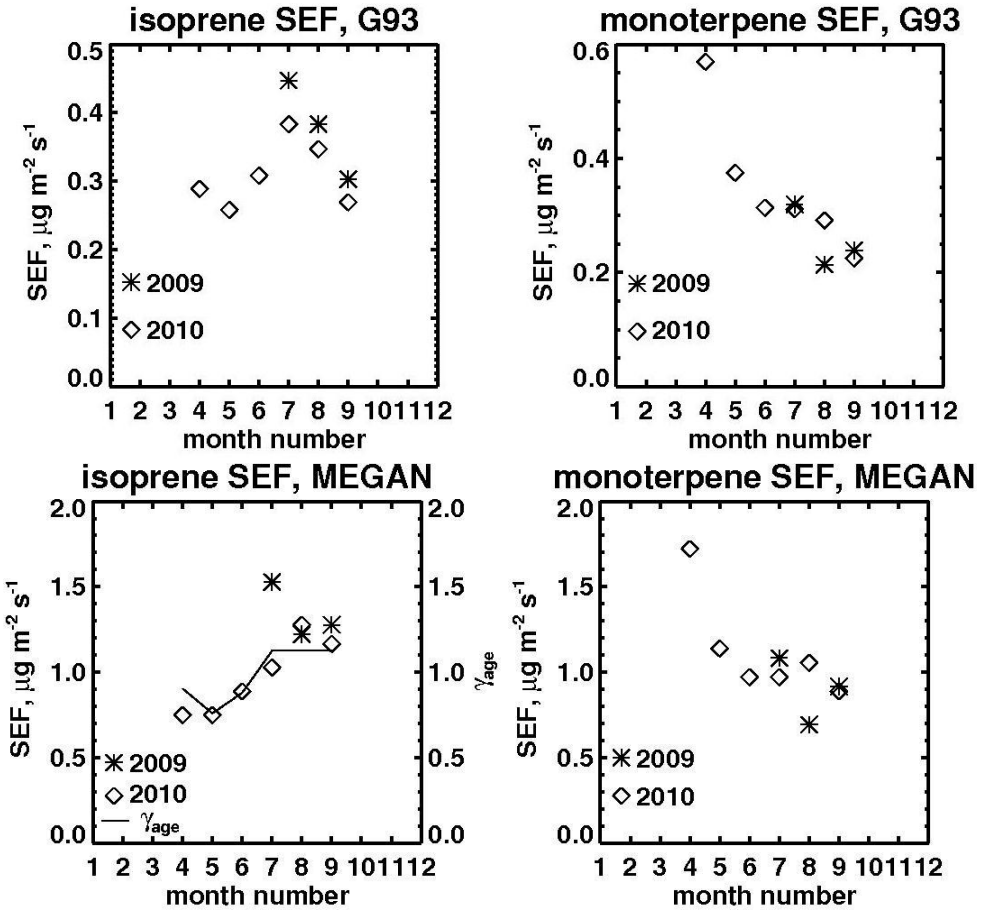


Figure 52: Monthly standard emission factors (SEF) for G93 (top) and MEGAN (bottom) in 2009 and 2010, as determined from the Vielsalm measurements and the model calculations using MOHYCAN.

Methanol

The emissions of methanol are modeled according to the recent MEGAN algorithm, which includes both light-dependent and light-independent components (Stavrakou et al., 2010). The deposition flux (often observed to be minor at many other sites) is crudely represented with a deposition velocity v_d(cm/s)=0.125·LAI. The use of this relatively weak deposition velocity leads to a large overestimation of the net methanol fluxes at the Vielsalm site (Figure). The implementation of a more detailed absorption/desorption model (see Sect. 4.4) would very probably improve the comparison, but requires further investigation. Interestingly, both the diurnal cycle and the day-to-day variability of the fluxes are well reproduced when considering only the positive (observed) fluxes (right panel of Figure), suggesting that the emission model and the standard emission factor (0.8 mg m^{-2} h^{-1} at standard MEGAN conditions) might be appropriate.

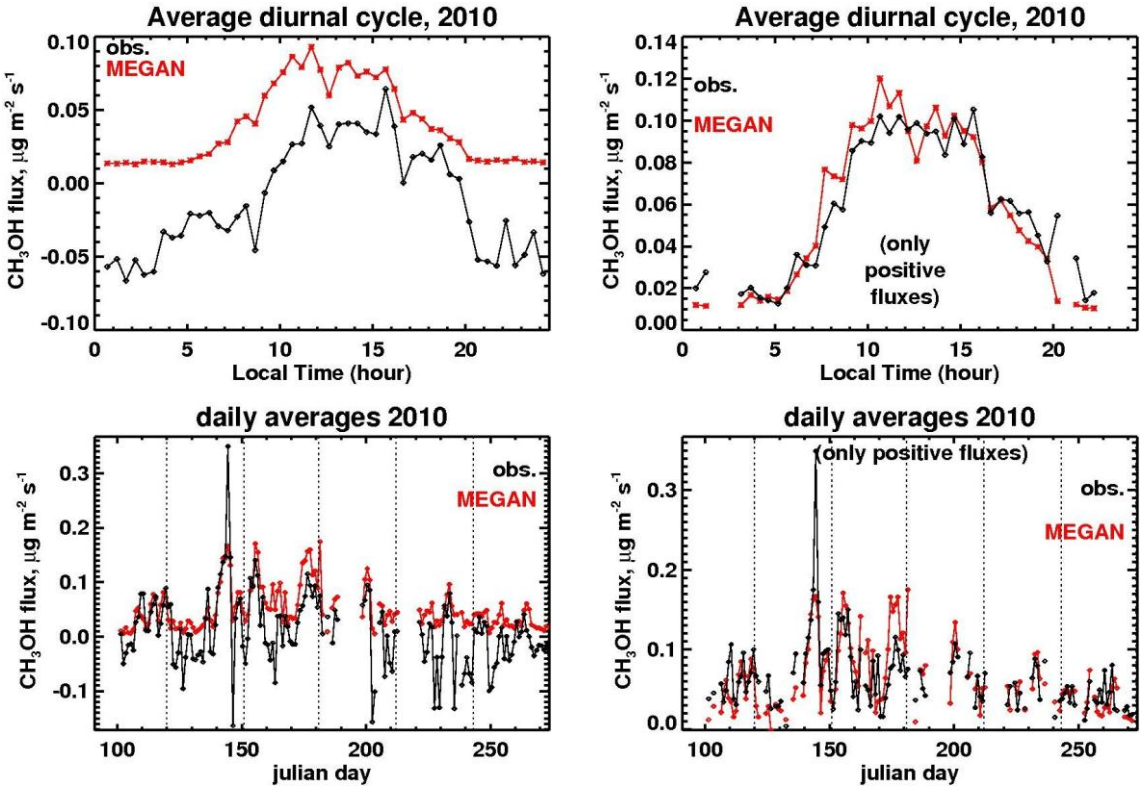


Figure 53 Average diurnal cycle of observed and modelled emissions in April-September 2010 (top), taking into account all measurements (left) or only positive measured fluxes (right); daily averaged emissions (bottom), taking into account all (left) or only positive measured fluxes (right).

3. Policy support

Policy makers bring the framework to have proper environmental living conditions for the people. In this sense they rely on scientific data to establish a proper policy for a healthy atmosphere. To that extent, European countries like Belgium are forced to make inventories about compounds emitted by mankind and nature that influence the atmospheric quality. It turns out that for the category of volatile organic compounds with quite different impacts such as contribution to tropospheric ozone formation, global warming and human toxicity, forests are quite important contributors. In this sense emission inventories of this group of compounds, i.e. biogenic volatile organic compounds (BVOCs), are essential in proper decision making. The emission inventories of BVOCs currently rely on models that are based on measurements and models from the early 1990s.

Our project results provide measurements and models that are a first step towards a better estimation of BVOC emissions. First, we learn that there are more factors than tree species, light and temperature that determine the emission of BVOCs. For example, seasonality, the physiological status of the leaves and infection influence the emissions. Second, we learn that a number of compounds are emitted which do not get proper attention in emission inventories and that may be of interest in further atmospheric chemistry, in particular in ozone formation and particulate matter development. In a further stage, these findings could be the base of a refined BVOC emission estimation providing a more sound basis for proper policy with respect to atmospheric quality.

If the preliminary relation of BVOC emissions and temperature (growth room experiment) will be confirmed by the canopy and stand level experiments, these results might have important consequences in the framework of global climate change, since models predict a further 1.5-5.5°C warming for this century as a results of increased atmospheric CO_2 and other trace gases concentrations (IPCC 2007). Thus, when ambient temperatures will rise, the monoterpenoid emissions will rise as well.

4. Dissemination and valorization

Results have been disseminated and valorized in different ways.
First, they have been disseminated in the international scientific community through publications in international peer reviewed journals (see section 5). Some paper have been already been published, others are accepted, under revision or in preparation.
Second, the results have been also communicated at international conferences through various oral and poster contributions (see section 5).
Third, through the follow-up committee meetings stakeholders – not only scientists but also public institutions such as the VMM (Vlaamse Milieumaatschappij, Afdeling Meetnetten en Onderzoek) and the "Ministère de la Région Wallonne, Direction Générale des Ressources Naturelles" have been informed about the results of the project.
Finally, results have not only been communicated to the scientific community but a more general public as well. The Impecvoc project has not only its website (www.impecvoc.ugent.be) and its flyer, but occasions where scientists of the consortium had events with a more broad public have been taken to expose the audience to the results of the Impecvoc project, e.g. at the occasion of the BISA open days (Brussels, October 6-7 October 2007), at the 'Studiedag starters in het bosonderzoek' (19 March 2009, Brussels), at the University Day at BISA (28 November 2008, Brussels), at the 'Opendeurdag Ghent University' (14 March 2009), and during the 'Wetenschapsweek' at Ghent University (23-24 Oktober 2008).

5. Publications

Peer reviewed publications

1. Bloemen J., Šimpraga M., Vanhaecke L.,Verbeeck H., Amelynck C., Schoon N., Demarcke M., Müller J-F., Dewulf J., Van Langenhove H., Joó É., Heinesch B., Aubinet M., Steppe K.. How do sun and shade leaves in European beech (Fagus sylvatica L.) influence volatile organic compounds emitted into the atmosphere? In preparation.
2. Deligne A., Heinesch B., Aubinet A. (2010). New transfer functions for correcting turbulent water vapour fluxes. Boundary-Layer Meteorology 137, 205-221.
3. Demarcke M, Amelynck C, Schoon N, Van Langenhove H, Dewulf J (2009). Laboratory studies in support of the detection of sesquiterpenes by Proton-Transfer-Reaction-Mass-Spectrometry. Int. J. Mass Spectrom. 279: 156-162.
4. Demarcke, M., Amelynck, C., et al. (2010). “Laboratory studies in support of the detection of biogenic unsaturated alcohols by proton transfer reaction-mass spectrometry”. International Journal of Mass Spectrometry 290, 14-21.
5. Demarcke, M., Müller, J.F., Schoon, N., Van Langenhove, H., Dewulf, J., Joó, E., Steppe, K., Simpraga, M., Heinesch, B., Aubinet, M., Amelynck, C., (2010). History effect of light and temperature on monoterpenoid emissions from Fagus sylvatica L. Atmospheric Environment 44, 3261-3268.
6. Joó É, Dewulf J, Amelynck C, Schoon N, Pokorska O, Šimpraga M, Steppe K, Aubinet M, Van Langenhove H. (2011) Constitutive versus heat and biotic stress induced BVOC emissions in Pseudotsuga menziesii. Atmospheric Environment 45, 3655-3662.
7. Joó É, Dewulf J, Demarcke M, Amelynck C, Schoon N, Müller J-F, Šimpraga M, Steppe K, Van Langenhove H. (2010) Quantification of interferences in PTR-MS measurements of monoterpene emissions from Fagus sylvatica L. using simultaneous TD-GC-MS measurements. International Journal of Mass Spectrometry 291, 90-95.
8. Joó É, Van Langenhove H, Šimpraga M, Steppe K, Amelynck C, Schoon N, Müller J-F, Dewulf J (2010). Variation in biogenic volatile organic compound emission pattern of *Fagus sylvatica* L. due to aphid infection. Atmospheric Environment 44, 227-234
9. Laffineur Q., Aubinet M., Schoon N., Amelynck C., Müller J.-F., Dewulf J., Van Langenhove H., Steppe K., Šimpraga M., Heinesch B. (2011). Isoprene and monoterpene emissions from a mixed temperate forest, Atmospheric Environment 45, 3157-3168.
10. Laffineur Q., Aubinet M., Schoon N., Amelynck C., Müller J.-F., Dewulf J., Van Langenhove H., Steppe K., Heinesch B., (2011). Abiotic and biotic control of methanol exchanges in a temperate mixed forest, accepted under minor revisions in Atmospheric Chemistry and Physics.

11. Müller J-F, Stavrakou T, Wallens S. De Smedt I, Van Roozendael M, Rinne J, Munger B, Goldstein A, Guenther A (2008). Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environmental model. Atmos. Chem. Phys. 8: 1329-1341.
12. Šimpraga M, Verbeeck H, Demarcke M, Amelynck C, Schoon N, Dewulf J, Van Langenhove H, Steppe, K, (2011). Comparing monoterpenoid emissions and net photosynthesis of beech (*Fagus sylvatica* L.) in controlled and natural conditions. Atmospheric Environment 45, 2922-2928.
13. Šimpraga M, Verbeeck H, Demarcke M, Amelynck C, Schoon N, Müller J-F, Joo É, Pokorska O, Dewulf J, Van Langenhove H, Heinsch B, Aubinet M, Laffineur Q, Steppe K, (2011). Clear link between BVOC, photosynthesis and radial stem growth in beech during drought stress. Atmospheric Environment 45, 2922-2928.
14. Šimpraga M, Verbeeck H, Jonckheere I,' Soubie, R, Heinsch B, Aubinet M, Caroline Vincke, Steppe K. Seasonal variation of LAI in the footprint of a flux measurement tower in Wallonia, Belgium. In preparation.
15. Šimpraga M, Verbeeck H, Pokorska O, Bloemen J, Amelynck C, Schoon N, Joo É, Dewulf J, Van Langenhove H, Heinsch B, Aubinet M, Steppe K, (2011). Seasonality of photosynthesis and BVOC emissions for anatomically different temperate tree species. Submitted.
16. Šimpraga M, Verbeeck H, Pokorska O, Bloemen J, Amelynck C, Schoon N, Joo É, Dewulf J, Van Langenhove H, Heinsch B, Aubinet M, Steppe K. Vertical gradient of photosynthesis and monoterpenoid emissions in a beech canopy under different sky conditions. In preparation.
17. Stavrakou T., Guenther A., Razavi A., Clarisse L., Clerbaux C., Coheur P.-F., Hurtmans D., Karagulian F., De Mazière M., Vigouroux C., Amelynck C., Schoon N., Laffineur Q., Heinesch B., Aubinet M., (2011). First space-based derivation of the global atmospheric methanol emission fluxes. Atmospheric Chemistry and Physics, 11, 4873-4898.

Presentations (oral presentation, posters, abstracts)

1. Amelynck C, Schoon N, Demarcke M, Dhooghe F, posters presented during the open days of BISA, Brussels, October 6-7 October 2007.
2. Amelynck C., Schoon N., Debie E. and Bultinck P. Ion/molecule reaction studies in support of the detection of sesquiterpenes by CIMS, in the Proceedings of the 3rd International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications (Obergurgl, Austria), pp. 127-131, Editors: A. Hansel, T.D. Märk, Innsbruck University Press, 2007.
3. Bloemen J, Šimpraga M, Verbeeck H, Amelynck C, Steppe K. 2009. Dynamische interactie tussen fotosynthese en BVOS emmissies in bosecosyetemen. Studiedag starters in het bosonderzoek, 19 March 2009, Brussel, Belgium.

4. Demarcke M, Amelynck C, Schoon N, Dewulf J and Van Langenhove H. Investigations on the influence of drift field and humidity on sesquiterpene product ion distributions in a PTR-MS instrument and implications for sesquiterpene detection sensitivity, in the Proceedings of the 4th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications (Obergurgl, Austria), pp. 170-173, Editors: A. Hansel, J. Dunkl, Innsbruck University Press, 2009.
5. Demarcke M, Amelynck C, Schoon N, Dewulf J, and Van Langenhove H. Characterization of Proton Transfer Reaction Mass Spectrometry for the detection of sesquiterpenes. Geophysical Research Abstracts, Vol. 11, EGU2009-4044, EGU General Assembly 2009, Vienna, Austria, April 19-24 2009.
6. Demarcke M, Amelynck C, Schoon N, Müller J-F, Joó É, Dewulf J, Van Langenhove H, Šimpraga M, Steppe K, Lemeur R and Samson R. Branch enclosure BVOC flux measurements from *Fagus sylvatica* L. in a natural forest environment: preliminary results. Geophysical Research Abstracts, Vol. 11, EGU2009-2344-4, EGU General Assembly 2009, Vienna, Austria, April 19-24 2009.
7. Demarcke M, Amelynck C, Schoon N, Müller J-F, Joó É., Dewulf J, Van Langenhove H, Šimpraga M, Steppe K, Samson R and Lemeur R. Measurements of BVOC emissions from *Fagus sylvatica* L. in controlled environmental conditions: preliminary results. Geophysical Research Abstracts, Vol. 10, CD-Rom EGU2008-A-02589, EGU General Assembly, Vienna, Austria, April 13-18 2008.
8. Demarcke M, Amelynck C, Schoon N, Müller J-F., Joó É., Dewulf J, Van Langenhove H, Šimpraga M, Steppe K, Samson R, Lemeur R, Aubinet M, Heinesch B. Impact of Phenology and Environmental Conditions on Biogenic Volatile Organic Compounds (BVOC) Emissions from Forest Ecosystems (IMPECVOC): preliminary results. University Day, BISA, Brussels, November 28 2008 (poster).
9. Demarcke M, Amelynck C, Schoon N, Müller J-F., Joó É., Dewulf J, Van Langenhove H, Šimpraga M, Steppe K, Laffineur Q., Heinesch B., Aubinet M, Effect of seasonality and short-term light and temperature history on monoterpene emissions from European beech (/Fagus sylvatica/ L.). Contributions to the 5th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications, 26 Jan - 2 Febr 2011, Obergurgl, Austria, Innsbruck University Press, Editors: A. Hansel, J. Dunkl.
10. Joó É, Dewulf J, Schietse L, Pokorska O, Šimpraga M, Steppe K, Amelynck C, Schoon N, Müller J-F, Aubinet M, Van Langenhove H. Seasonal study on BVOC emissions from Douglas-fir measured by GC-MS. Gordon Research Conference 2010, Les Diablerets, Switzerland, May 23-28 2010 (poster presentation).

11. Joó É, Pokorska O, Van Langenhove H, Dewulf J. Measurement of biogenic volatile organic compounds from forest ecosystems. Opendeurdag Ghent University, 14 March 2009.
12. Joó É, Van Langenhove H, Schietse L, Pokorska O, Šimpraga M, Steppe K, Demarcke M, Amelynck C, Schoon N, Müller J-F, Samson R. and Dewulf J. Changes in BVOC emission pattern from *Fagus sylvatica* L. measured by thermal desorber GC-MS. Geophysical Research Abstracts, Vol. 11, EGU2009-672-2, EGU General Assembly 2009, Vienna, Austria, April 19-24 2009.
13. Joó É, Vandermeersch L, De Roo K, Dewulf J, Van Langenhove H. Geuren natuurlijk: De geur van bomen. Wetenschapsweek, 23-24 Oktober 2008.
14. Joó É., Dewulf J., Amelynck C., Schoon N., Pokorska O., Šimpraga M., Steppe K., Aubinet M., Van Langenhove H. Effect of heat and biotic stress on the emission of *Pseudotsuga menziesii* (Douglas-fir). Integrated Land Ecosystem-Atmosphere Processes Study (iLEAPS) conference and workshop, Garmisch-Partenkirchen, Germany, 16-23 September 2011.
15. Laffineur Q. Flux de Composés Organiques Volatils (COV) au-dessus d'une forêt belge: De la mesure par eddy covariance à la recherche des mécanismes d'émission et de déposition. Invited scientific presentation. Nancy, France, 16 September 2010.
16. Laffineur Q., Heinesch B., Aubinet M., Schoon N., Amelynck C., Müller J.-F., Dewulf J., Van Langenhove H., Joó E., Steppe K. VOC emissions from a temperate mixed forest in Belgium measured by eddy-covariance. Geophysical Research Abstracts Vol. 12, EGU2010-14283-1, EGU General Assembly 2010, Vienna, Austria, May 2-07 2010.
17. Laffineur Q., Heinesch B., Aubinet M., Schoon N., Amelynck C., Müller J.-F., Dewulf J., Van Langenhove H., Joó E., Steppe K., Aubinet M. What can we learn from year-round BVOC disjunct eddy-covariance measurements? A case example from temperate forest. Contributions to the 5th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications, 26 Jan – 2 Febr 2011, Obergurgl, Austria, Innsbruck University Press, Editors: A. Hansel, J. Dunkl, 45-49.
18. Rimetz-Planchon J, Dhooghe F, Schoon N, Vanhaecke F Amelynck C. Application of Chemical Ionization by H_3O^+ or NO^+ and subsequent Collision Induced Dissociation of major product ions to selective on-line detection of sesquiterpenes and monoterpenes. Contributions to the 5th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications, 26 Jan – 2 Febr 2011, Obergurgl, Austria, Innsbruck University Press, Editors: A. Hansel, J. Dunkl, 199-202.
19. Šimpraga M, Steppe K, Demarcke M, Amelynck C, Schoon N, Joó É., Dewulf J, Van Langenhove H, Samson R, Müller J-F. and Lemeur R. Preliminary observations of temperature effects on carbon loss through BVOC emissions in *Fagus sylvatica* L. Geophysical Research Abstracts, Vol. 10, CD-Rom EGU2008-A-09084, EGU General Assembly, Vienna, Austria, April 13-18 2008.

20. Šimpraga M., Steppe K., Demarcke M., Amelynck C., Schoon N., Samson R., Lemeur R. How does drought stress in a potted beech tree affects the relationship between photosynthesis and BVOC emissions? Studiedag starters in het bosonderzoek, 19 March 2009, Brussel, Belgium.
21. Šimpraga M., Steppe K., Verbeeck H., Lemeur R. The IMPECVOC project (Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems). CES newletter. Center of Environmental Sanitation, Ghent University. 2009.
22. Šimpraga M., Verbeeck H., .Jonckheere I., Heinsch B., Laffineur Q., Aubinet M., Steppe K. Spatial and seasonal variation of LAI in the footprint of a flux measurement tower. March 2011. Starters in Bosonderzoek conference. (oral presentation)

Master theses

1. Gregoire, M., (2011). Etude des flux biogéniques d'acétone entre une forêt tempérée et l'atmosphère. Gembloux Agro-Bio Tech. Gembloux, Université de Liège. Master Thesis: 69 pp.
2. Van den Bossche, J., (2011) Modellering van BVOC emissies van een gemengd bosecosysteem, Master thesis, 77 pp.
3. Hoffelt, T., (2010). Contrôle environnemental et physiologique des flux de composés organiques volatiles oxygénés échangés par une forêt mixte de Vielsalm. Gembloux Agro-Bio Tech. Gembloux, Université de Liège. Master Thesis: 69 pp.
4. Schietse, L., (2009) Emission of biogenic volatile organic compounds from European beech related to biotic stress and from Dougles fir subjected to varying environmental conditions, Master thesis, 87 pp.
5. Bloemen, J., (2009) Dynamische interactie tussen fotosynthese en BVOS emissies in bosecosystemen (Dynamical interaction between photosynthesis and BVOC emissions in the forest ecosystems), Master thesis, 113 pp.
6. Neina, D., (2008) Biogenic volatile organic compounds from some tree species, Master thesis, 87 pp.

PhD dissertations

1. Demarcke, M., (2011). Contribution to the characterization of proton transfer reaction-mass spectrometry (PTR-MS) for biogenic volatile organic compound (BVOC) detection and its application to *Fagus sylvatica* L. for emission model evaluation. Ghent University. PhD dissertation. 158p.
2. Joó, É., (2011). Characterization of stress induced changes in biogenic volatile organic compound (BVOC) emissions from *Fagus sylvatica* and *Pseudotsuga menziesii*. Ghent University. PhD dissertation. 139p.

3. Pokorska, O., (2012) Biogenic volatile organic compound analysis from selected European deciduous and coniferous tree species: composition and emission rate, submitted.
4. Laffineur, Q., (2012) in prepration.
5. Šimpraga, M., (2012) in preparation.

6. Acknowledgements

We acknowledge financial support from the Flemish Government for the MAT 95XPTrap in the framework of the Flemish investment support for heavy research equipment. We would like to especially thank Prof. Luc Tirry for his kind support in identifying the aphid Phyllaphis fagi L., and Prof. Monica Höfte and Jasper Devlamynck for their kind effort to identify the disease on the *P. menziesii.* We are grateful for all the outstanding technical supports that helped to establish the measurements.

7. References

Bertin et al., Oecol. 107 (1996) 456 – 462.
De Swaef et al., Agricultural water management (2009) 541-55.
Dindorf et al., J. Geophys. Res. 111 (2006) D16305, doi : 10.1029/2005JD006751
Dominguez-Taylor, Atmos. Environ. 41 (2007) 2780-2790.
Filella et al., Physiologia Plantarum 130 (2007) 58-66.
Graus et al., Plant Phys. 135 (2004) 1967-1975.
Grote and Niinemets, Plant Biology. 10 (2007) 8-19.
Guenther et al., Atmos. Chem. Phys. 6 (2006) 3181-3210.
Guenther et al., J. Geophys. Res. 98 (1993) 12609-12617.
Guenther, Ecol. Appl. 7 (1997) 34-45.
Harley et al., Tree Physiology 16 (1996) 25-32.
Helmig, Atmos. Environ. 40 (2006) 4150-4157.
Holzke et al., J. Atm. Chem. 55 (2006) 81-102.
IPCC 2007. Observed and projected changes in climate as they relate to water. Intergovernmental Panel on Climate Change.
Jonckheere et al., Agri. Forest Meteo. 121 (2004) 19-35.
Kahl et al., Phytochemistry 51 (1999) 383-388.
Karl et al., Science **330**(6005): (2010) 816-819.
Kesselmeier, Atmos. Chem. Phys. Disc. 4 (2004) 528530.
Liakakou, Atmos. Environ. 41, (2007) 1002-1010.
Liss and Slater, Nature 247 (1974) 181-184.
Loreto et al., Plant Cell and Env. 29 (2006) 1820-1828.
Monsi and Saeki, Jap. J. of Bot. 14 (1953) 22-52.
Monson et al., Atmos. Environ. 29 (1995) 2989-3002.
Moukhtar et al. Science of The Total Environment 354 (2006) 232-245.
Moukhtar et al., Atm. Env. 39 (2005) 3535-3547.
Ormeno, Atmos. Environ. 41 (2007) 629-639.
Sarijeva et al., Journal of Plant Physiology 164 (2007) 950–955.
Schuh et al., J. Atm. Chem. 27 (1997) 291-318.
Shabanov et al., Report, Uni. Maryland, 2007.
Sharkey et al., Oecol. 95 (1993) 328-333.
Soubie et al., EGU General Assembly, Vienna, 2010.
Spirig et al., Atmos. Chem. Phys., 5 (2005) 465-481.
Stavrakou et al. Atmos. Chem. Phys. (submitted).
Sutton et al., Atmos. Env. 32 (1998) 473-480.
Tiiva, Atmos. Environ. 41 (2007) 3819-3828.
Tollsten et al., Phytochem. 43 (1996) 759-762.
Vande Walle, PhD dissertation (2007) Ghent University.
Wallens, S., PhD Thesis, Université Libre de Bruxelles, Brussels, 2004.