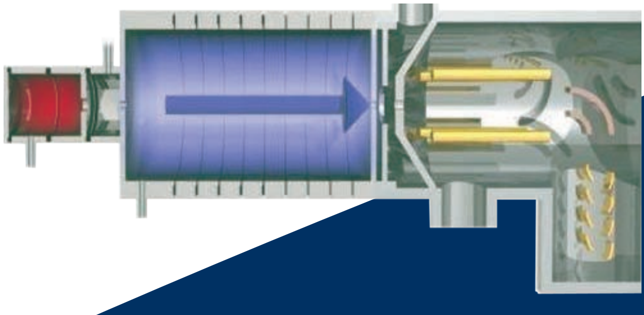
CONFERENCE SERIES

Armin Hansel, Jürgen Dunkl

Contributions

5th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications



innsbruck university press

CONFERENCE SERIES

innsbruck university press

Armin Hansel
Jürgen Dunkl
Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

Local Organizing Committee:
Armin Hansel
Sandra Naschberger
Martin Breitenlechner
Jürgen Dunkl

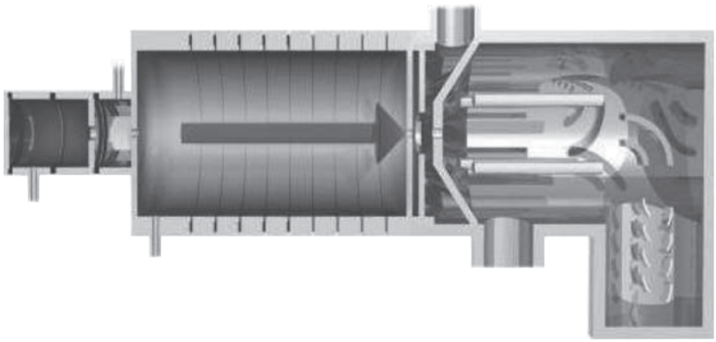
Universität Innsbruck, Vizerektorat für Forschung
1st edition

Cover design: Carmen Drolshagen
Produced: Fred Steiner, Rinn – Book on Demand

www.uibk.ac.at/iup

ISBN 978-3-902719-88-1

5th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications



Contributions

Editors:

Armin Hansel

Jürgen Dunkl

Institut für Ionenphysik und Angewandte Physik
der Leopold-Franzens-Universität Innsbruck
Technikerstr. 25
A-6020 Innsbruck, Austria

Obergurgl, Austria

January 26th – February 2nd, 2011

Effect of seasonality and short-term light and temperature history on monoterpene emissions from European beech (*Fagus sylvatica* L.)

M. Demarcke[1], C. Amelynck[1], N. Schoon[1], J.-F. Müller[1], E. Joó[2], J. Dewulf[2], H. Van Langenhove[2], M. Šimpraga[3], K. Steppe[3], Q. Laffineur[4], B. Heinesch[4] and M. Aubinet[4]

[1] *Belgian Institute for Space Aeronomy, Brussels, Belgium, crist.amelynck@aeronomie.be*

[2] *Research Group Environmental Organic Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium*

[3] *Laboratory of Plant Ecology, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium*

[4] *Gembloux Agro-Bio Tech, Unité de Physique des Biosystèmes, University of Liège, Gembloux, Belgium*

Abstract

Branch enclosure measurements of monoterpene emission rates have been performed at different positions in the canopy of a European beech tree in natural environmental conditions. Strong and position-dependent standard emission rate variations were observed in the course of the growth season. By using the obtained dataset and a modified version of the MEGAN algorithm, the response of the emissions to short-term light and temperature history was investigated.

Introduction

Monoterpenes ($C_{10}H_{16}$) are a class of highly reactive non-methane volatile organic compounds (NMVOC) emitted by terrestrial vegetation, with estimated global emission rates between 32 and 127 Tg C yr^{-1} [1]. Because of their impact on the budget of atmospheric oxidants and their role as precursors of secondary organic aerosols, more accurate monoterpene emission rate estimates are clearly required. *Fagus Sylvatica* L. trees (European beech) are known to be high emitters of *de novo* synthesized monoterpenes [2,3,4], which can be described by the light- and temperature dependent emission algorithms that were developed for isoprene [5,6]. Next to the response of BVOC emissions to instantaneous light (PPFD) and leaf temperature, the recently developed MEGAN algorithm [6] also considers the role of other factors such as leaf age (seasonality), soil moisture availability and the average PPFD and leaf temperature over the past 24 hours (short-term history) and over the past 10 days (long-term history). Seasonality of monoterpene emissions from BVOCs was already considered by Holzke et al. to some extent [4], but the results of the present work show that temporal variation of the monoterpene standard emission rate also strongly depends on the position of the leaves in the canopy. The effect of short-term light- and temperature history has already been studied for young Fagus sylvatica L. saplings at controlled growth chamber conditions [7] and this study has now been extended for an adult tree in natural environmental conditions.

Experimental Methods

Monoterpene emissions from four branches at different positions in the canopy of an 85 year old *Fagus sylvatica* L. tree in an experimental forest (Gontrode, Belgium, 50°59'N, 3°47'E) were measured using PFA branch enclosures, which were continuously supplied with dust-, ozone- and VOC-free ambient air (4 L min^{-1}). Two enclosed branches were located in the upper canopy and are designated as the sunlit and semi-shaded branches. The branches in the middle and lower canopy correspond to deep shade conditions. All enclosures were provided with PPFD, leaf and air temperature and relative humidity sensors. Measurements were performed from early May to the end of September 2008, with the exception of the month of July. Part of the BVOC-enriched air leaving the enclosures was pumped through individual, thermally insulated and slightly heated PFA tubes towards a manifold located in a cabin at the bottom of a measurement tower providing access to the branches. In the cabin the enclosure air was analyzed for BVOCs with a hs-PTR-MS instrument and for H_2O and CO_2 exchange with an IRGA. Occasionally, air samples were taken from the enclosures for off-line BVOC analysis with TD-GC-MS. Two empty enclosures were used to determine the background values. The PTR-MS ion signal at m/z 137 was used to quantify monoterpenes and the PTR-MS was calibrated regularly by using a gravimetrically prepared dilute mixture of BVOCs in N_2 (Apel-Riemer Inc., CO, USA). The G97 [5] and MEGAN [6] algorithms were evaluated against the experimentally determined emission rates. In order to decrease the discrepancy between the model estimations and the observations, the original MEGAN model was modified in such a way that the number of hours (n) taken into account in the short-term light- and temperature history terms, the factors describing the importance of past PPFD and temperature conditions (λ_1 and λ_2) and the factor controlling light-saturation of the emissions (λ_3) were treated as variables (in contrast to MEGAN where these values were set to 24, 1, 1 and 1, respectively) and were estimated by minimizing the cost between the modified MEGAN model and the experimental data.

Results and Discussion

Whereas the leaf temperature didn't show much variation, incident PPFD values differed greatly between the four branches, with median noon values ranging from 350 and 40 µmol m^{-2} s^{-1} (for the sunlit and semi-shaded branch, respectively) to below 15 µmol m^{-2} s^{-1} for deep shade conditions. Emissions from the enclosed branches in the middle and lower canopy were most of the time below the detection limit. For both branches in the upper canopy, the highest emissions were obtained in early May, shortly after budbreak. Whereas the Standard Emission Factor (SEF value according to G97) for the sunlit branch already started to decrease drastically at the beginning of the growth season, the one of the semi-shaded branch showed a more constant behavior and a clear decline was not observed until September 9th. These results clearly show that the position of the branches in the canopy, which determines leaf morphology and physiology, has a large influence on monoterpene emission rates.

In agreement with previous studies [7], the observed emissions, corrected for T-dependence (through division by the T-related terms in the G97 and MEGAN algorithms), showed a hysteretic behavior as a function of PPFD, with higher values in the afternoon than in the morning. This points towards a dependence of the emissions on the average PPFD values of the past n hours with $n < 24$.

Diurnally averaged monoterpene emission rates from the semi-shaded branch in early May and in August-September are shown in Figure 1. A clear discrepancy can be noticed between the observations and the calculated emission rates according to the G97 and the MEGAN algorithm. A better agreement was obtained when calculating the emission rates with the modified MEGAN algorithm. Whereas a single set of values for the added parameters in the modified algorithm was sufficient to considerably improve emission estimates during the period from the end of May to the end of September, a significant improvement of the emission rate estimation for early May required a separate set of optimal values. By further dividing the measurement period into subperiods, and by optimizing the added parameters for each of these subperiods, an attempt was made to investigate the seasonal evolution of the optimal values for these parameters for the sunlit and semi-shaded branch.

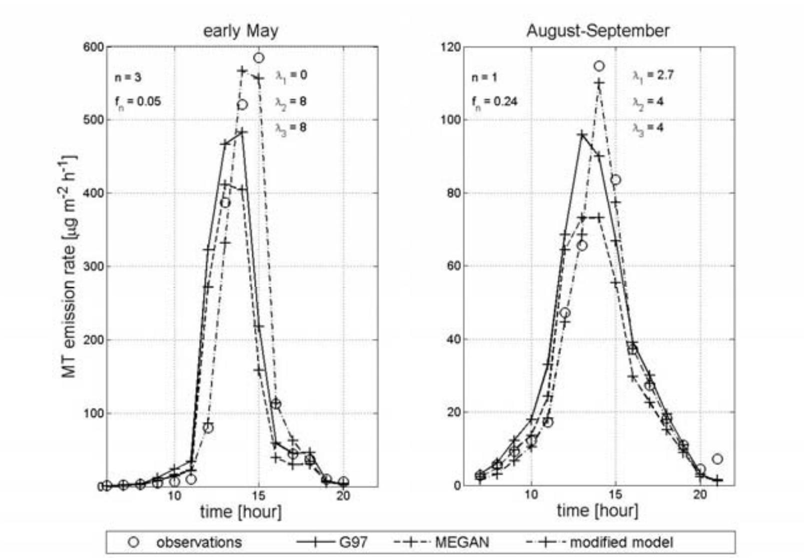


Figure 1: Observed and modeled diurnally averaged monoterpene emission rates for the semi-shaded branch during early May and August-September.

Acknowledgements

The authors wish to acknowledge support from the Belgian Federal Science Policy Office in the framework of the project “Science for a Sustainable Development: Terrestrial Ecology” (IMPECVOC, contract #SD/TE/03B) and the “FWO-Vlaanderen” (contract # G.0031.07).

References

[1] A. Arneth, R.K. Monson, G. Schurgers, U. Niinemets, P.I. Palmer, Why are estimates of global terrestrial isoprene emissions so similar (and why is this not so for monoterpenes) ? Atmospheric Chemistry and Physics 8, 4605-4620, (2008).

[2] T. Dindorf et al., Significant light and temperature dependent monoterpene emissions from European beech (*Fagus sylvatica* L.) and their potential impact on the European volatile organic compound budget. Journal of Geophysical Research 111, D16305. doi:10.1029/2005/JD006751, (2006).

[3] S. Moukhtar, B. Bessagnet, L. Rouil, V. Simon. Monoterpene emissions from Beech (*Fagus sylvatica*) in a French forest and impact on secondary pollutants formation at regional scale. Atmospheric Environment 39, 3535-3547, (2005).

[4] C. Holzke, T. Dindorf, J. Kesselmeier, U. Kuhn, R. Koppmann, Terpene emissions from European beech (*Fagus sylvatica* L.): pattern and emission behaviour over two vegetation periods. Journal of Atmospheric Chemistry 55, 81-102, (2006).

[5] A. Guenther, Seasonal and spatial variations in natural volatile organic compound emissions, Ecological Applications 7, 34-45, (1997).

[6] A. Guenther et al., Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmospheric Chemistry and Physics 6, 3171-3210, (2006).

[7] M. Demarcke et al., History effect of light and temperature on monoterpenoid emissions from *Fagus sylvatica* L., Atmospheric Environment 44, 3261-3268, (2010).