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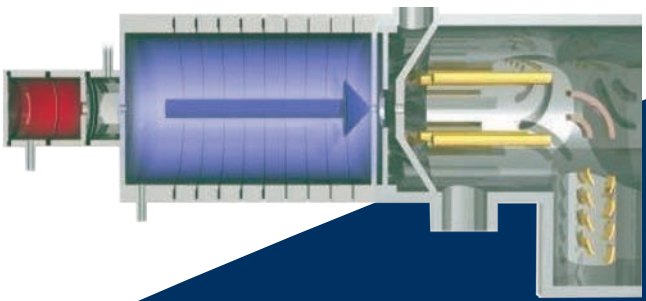

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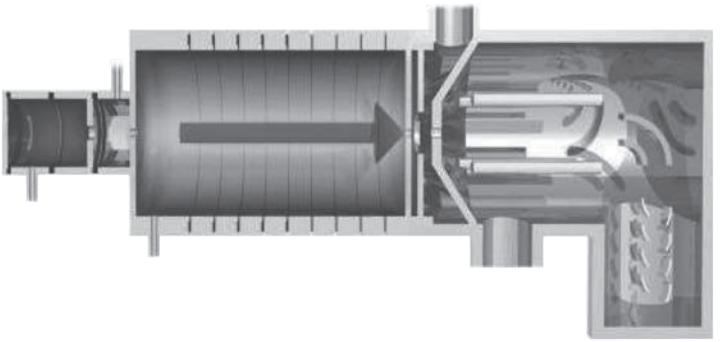

Contributions

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What can we learn from year-round BVOC disjunct eddy-covariance measurements? A case example from temperate forest.

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Abstract

Long term ecosystem-scale biogenic volatile organic compounds (BVOC) flux measurements by disjunct eddy-covariance are needed to determine and characterize the BVOC emissions/depositions from episodic events (budburst, stress) as well as the continuous emission/deposition during vegetation growth and its seasonal evolution in interaction with climate and environment. If the data coverage is sufficient, this technique has the potential to provide a dataset covering the whole spectrum of meteorological and phenological conditions encountered by the studied ecosystem ending in a statistically more robust dataset than what can be provided by other BVOC measurement techniques. In addition, long term measurements allow in Oxygenated VOCs (OVOCs) depositions to be estimated in a realistic manner with is not the case with the enclosure technique.

Here we present a year-round campaign of disjunct eddy-covariance BVOC fluxes above a mixed temperate forest performed in the frame of the IMPECVOC (Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems) project. We will analyse the three main BVOC species (isoprene/monoterpenes and methanol) in order to illustrate the interest of long-term flux measurements by investigating the main driving variables and the underlying mechanisms of emission/deposition, how *de novo* carbon allocation to the isoprene/monoterpenes skeleton structure is altered through the time. For methanol, we will show the importance of deposition on a long-term basis and use an empirical model to discriminate the physical and physiological components of the exchange.

Introduction

Global BVOCs emission rates by terrestrial vegetation are estimated to be 700-1000 TgC y^{-1} [1] corresponding to nearly 90% of global VOC emissions. These emissions represent a major source of reactive carbon to the atmosphere that can influence the level of tropospheric ozone, the lifetime of other chemical compounds such as methane and the production of secondary organic aerosols, which can have both direct and indirect influence on the Earth's radiative budget [2].

Large uncertainties on global BVOC emission estimations result from the incomplete understanding of emission/deposition mechanisms depending on climate, environment and

vegetation physiology. BVOC emission measurements at different level scales (leaf, branch, ecosystem) are mostly limited in time, are operated during good climatic conditions and rarely cover the seasonal evolution. The best technique for long-term monitoring BVOC emissions in real conditions and at the ecosystem scale without disturbing the ecosystem is the disjunct eddy-covariance used in this study. In addition, the BVOC fluxes are measured simultaneously with carbon dioxide fluxes, which provide valuable information to better understand the BVOC production mechanisms. Our dataset extends from July to October 2009 and from April to October 2010 thus covering the Belgian spring, the summer and the first part of autumn. With this large data set, we have tried to extract the mechanisms of BVOC emission/deposition in relation with the seasonal evolution of vegetation.

Experimental Methods

Measurement site

The forested site is at Vielsalm in the Belgian Ardenne forest (50°18'18.20''N, 5°59'53.15''E altitude: 450 m). The climate is temperate maritime. The vegetation is a mixture of coniferous species, mainly Douglas fir (*Pseudotsuga menziesii* [Mirb.] Franco), Norway spruce (*Picea Abies* [L.] Karst.), Silver fir (*Abies alba* Miller), and deciduous species, mainly beeches (*Fagus sylvatica* L.).

Methodology

The technique used to measure ecosystem BVOC fluxes was the disjunct eddy-covariance (DEC) [3]. The flux was computed as the covariance of vertical wind velocity component (measured by a sonic anemometer at a sampling frequency of 20.8 Hz) and BVOC concentration measured by PTR-MS. The ion signal intensities of the masses of interest were measured in a cyclical way, ending in a disjunct concentration time series for each mass. We measured the ion signals at mass-to-charge (*m/z*) ratios 21, 33, 39, 45, 59, 69, 71, 81, 87 and 137. The dwell time for each mass was 0.2 s, ending in a 2 s measurement cycle length. The PTR-MS was operated at a drift tube pressure of 2.1 hPa, a drift tube temperature of 333 K and a drift voltage of 600 V, resulting in an E/N of 143 Townsend (1 Td = 10^{-17} V cm^2). During the measurements, the instrumental background was determined every 4 hours. The sensitivity of the instrument was calibrated for the main target compounds (isoprene, sum of monoterpenes, methanol, acetone and acetaldehyde) every two or three days using a gravimetrically prepared mixture of these gases in N_2.

The sonic anemometer was placed at the top of a tower at a height of 52 m. Ambient air was continuously sampled close to the sonic anemometer through a main sampling line (PFA tubing) 60 m long and 6.4 mm inner diameter and was slightly heated above ambient temperature. A part of this air flow was drawn into the PTR-MS through a 1.2 m long heated capillary inlet line (333 K) with an inner diameter of 1 mm. The time lag of the tube sampling was about 14.8 s. Measurements of turbulent CO_2 flux and relevant meteorological variables were also performed every half an hour.

Results and discussion

Up to now, we have investigated the isoprene/monoterpenes fluxes between July and September 2009. We have also studied the methanol fluxes and developed a model to better understand the physical and physiological mechanisms controlling the emission/deposition.

Isoprene/monoterpenes

During the day, isoprene and monoterperne 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 1), probably linked to acclimation or senescence. 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.

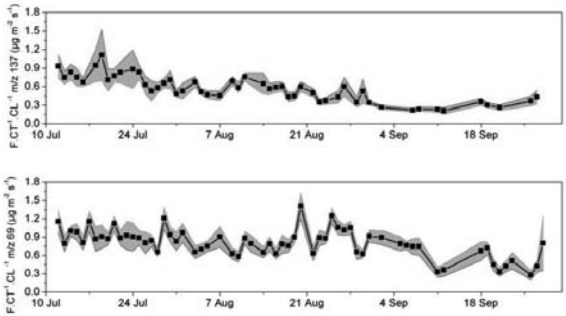

Figure 1: Mean diurnal evolution (PPFD > 300 µmol m−2 s−1) of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized for temperature (30°C) and PPFD (1000 µmol m−2 s−1). The grey area represents the 95% confidence intervals.

During the night, a slight positive flux of monoterpenes was observed that seemed to be driven by air temperature. These night emissions were probably due to the volatility of monoterpenes stored in the needle resin ducts of coniferous species. There could also be a contribution from the soil through litter decomposition, from roots or from micro-organisms. The standard emission factor (30°C) for night-time monoterpene fluxes was equal to 0.093 ± 0.019 µg $m^{-2}s^{-1}$.

Finally, we studied the seasonal evolution of the relationship between the gross primary production and the isoprene/monoterpene fluxes. A linear relationship was observed, highlighting the strong link between carbon assimilation and isoprene/monoterpene emissions (figure 2).

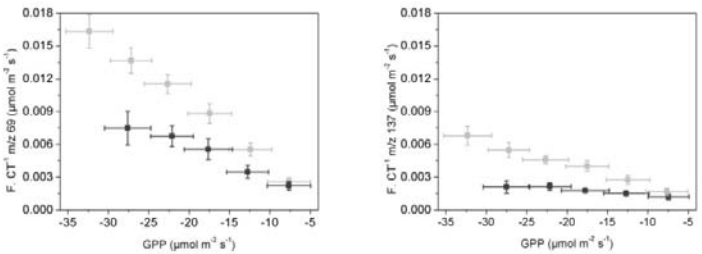

Figure 2: Bin averages of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized at 30°C (n≥14, error bars are 95% confidence intervals) in relation to the gross primary production (GPP) for July (light grey) and September (dark grey).

Methanol

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 closed to saturation. 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.

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) [4]. It took atmospheric methanol concentration, friction velocity, water vapor pressure deficit 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, as well in summer-autumn 2009, as during summer 2010. This suggests that, most of this time, the measured fluxes (night and day) can mainly be explained largely by a physical absorption/desorption process. In contrast, during one 2010 spring week, significant differences appeared between simulation and measurements (figure 3), suggesting the pre-eminence of biogenic fluxes. 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.

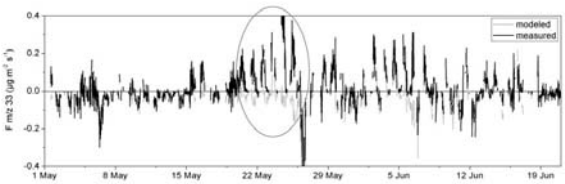

Figure 3: Representation of measured and modelled fluxes of methanol (m/z 33) during May-June 2010 period.

Acknowledgements

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References

[1] J. Lathière, D.A. Hauglustaine, A.D. Friend, N. De Noblet-Ducoudré, N. Viovy, G.A. Folberth, Impact of climate variability and land use changes on global biogenic volatile organic compound emissions, Atmospheric Chemistry and Physics 6, 2129-2146, (2006).

[2] J. Peñuelas, M. Staudt, BVOCs and global change, Trends in Plant Science 15, 133-144, (2010).

[3] Q. Laffineur, B. Heinesch, N. Schoon, C. Amelynck, J.-F. Müller, J. Dewulf, H. Van Langenhove, K. Steppe, M. Šimpraga, M. Aubinet, Isoprene and monoterpene emissions from a mixed temperate forest, Atmospheric Environment, submitted.

[4] P.S. Liss, P.G. Slater, Flux of Gases across the Air-Sea Interface, Nature 247, 181-184, (1974).