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Impact of diffuse light on isoprene and monoterpene emissions from a mixed temperate forest

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HIGHLIGHTS

- Isoprene/monoterpene emissions were measured continuously at the canopy scale.
- Isoprene/monoterpene emissions were studied under clear sky and cloudy conditions.
- The relationship between emissions/radiation and emissions/GPP were analysed.
- Under cloudy conditions, emissions were higher than under clear sky conditions.
- The enzymatic activity (canopy) was suggested to be lower under cloudy conditions.

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ABSTRACT

This study investigated the impact of diffuse light on canopy scale emission of isoprene and monoterpenes measured continuously above a mixed temperate forest, using the disjunct eddy-covariance by mass scanning technique with a proton transfer reaction-mass spectrometer (PTR-MS) instrument. To assess this impact, the relationship between emissions/radiation and emissions/gross primary production (GPP) under clear sky and cloudy conditions were analysed.

Under cloudy conditions (high proportion of diffuse radiation), the isoprene and monoterpene fluxes were enhanced compared to clear sky conditions (low proportion of diffuse radiation) at equivalent temperature and above-canopy total radiation. The whole-canopy enzymatic activity of the metabolic isoprene production pathway, however, was suggested to be lower under cloudy conditions than under clear sky conditions at equivalent temperature. The mechanisms behind these observations are probably linked to the better penetration of diffuse radiation in the canopy. Shade leaves/needles receive more radiation in cloudy conditions than in clear sky conditions, thereby inducing the observed effects.

1. Introduction

Biogenic Volatile Organic Compounds (BVOCs) emitted by terrestrial vegetation, particularly forests, dominate the global BVOC emissions. Forest ecosystems release mainly isoprene and monoterpenes into the atmosphere even if other chemical species, such as methanol, acetone, aldehydes and organic acids, are now also recognized to be emitted in large quantities by terrestrial vegetation (Lathière et al., 2006). The global isoprene and monoterpene emissions have been estimated at 412–601 Tg C yr^{-1} and 30–128 Tg C yr^{-1} (Arneth et al., 2008), respectively, representing the main BVOC emissions. Isoprene and monoterpenes play an important direct role in tropospheric chemistry and an indirect role in the Earth's radiation budget. Their oxidation products are important precursors for ozone (O_3) production/destruction, depending on the nitrogen oxide (NO_x) concentration (Atkinson and Arey, 2003). The atmospheric reactions of isoprene and monoterpenes can also have an important influence on the tropospheric concentration of hydroxyl (OH) radicals, thereby influencing the atmospheric lifetime of methane (Ortega et al., 2007).

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In addition to their importance in tropospheric gas phase chemistry, isoprene and monoterpene oxidation initiates and favours the production of compounds that can partition into the particulate phase, forming secondary organic aerosols (SOAs) (Hallquist et al., 2009; Kanakidou et al., 2005). SOAs have both a direct and indirect effect on atmospheric radiation. The direct effect is caused by the scattering and absorption of solar radiation by SOAs, whereas the indirect effect derives from their important role in the growth of cloud condensation nuclei. The total budget of SOAs formed in the atmosphere is also very uncertain, with estimates published in the literature ranging from 12 to 1640 Tg yr^{-1} (Pierce et al., 2012). The uncertainties about the SOA and isoprene/monoterpene budgets could be due partly to the potential feedback between the terrestrial biosphere, atmospheric aerosols and climate (Carslaw et al., 2010). The main driver of this feedback is the strong control that climate exerts over the emission of BVOCs. Increases in temperature are likely to lead to increased BVOC emissions (Fuentes et al., 2000; Šimpraga et al., 2011) and aerosol concentrations, resulting primarily in increased aerosol radiative cooling and a potential negative feedback mechanism (Carslaw et al., 2010; Kulmala et al., 2004). Aerosols and clouds can also affect the functioning of the biosphere in terms of its effect on canopy photosynthesis by increasing the relative proportion of diffuse radiation at the Earth's surface. Carbon sequestration in the canopy is enhanced under conditions where there is a high proportion of diffuse radiation compared with conditions with the same above-canopy total radiation but with a lower proportion of diffuse radiation (Gu et al., 2002; Knohl and Baldocchi, 2008). Since the metabolic production pathways of isoprene and monoterpenes are closely linked to photosynthesis (Lichtenthaler et al., 1997), an increase in diffuse radiation could also increase isoprene and monoterpene emissions at the same temperature. This opportunity hypothesis was mentioned briefly by Sharkey et al. (1991), but no ecosystem-scale micrometeorological measurements of BVOCs conducted to date have shown this effect. At a global scale, this latter effect could partly compensate for the aerosol radiative cooling effect on global BVOC emissions, but probably does not mask it because temperature is the main driver of BVOC emissions.

Our objective was to investigate the impact of the light regime (proportion of diffuse radiation) on canopy scale emissions of isoprene and monoterpenes without any artificial disturbance to the emissions and over the whole vegetation season. For this purpose, we used an eddy-covariance dataset of isoprene, monoterpene and CO_2 fluxes measured at stand level in a temperate forest. In order to highlight the behaviour of canopy emissions under different radiation regimes, the dataset was divided into two classes: clear sky conditions and cloudy conditions and the relationship between emissions/radiation and emissions/gross primary production (GPP) were analysed for these two datasets.

2. Material and methods

2.1. Measurement site

The experimental site is a forest ecosystem at Vielsalm in the Belgian Ardenne forest (50°18′18.20″N, 5°59′53.15″E; altitude 450 m). Its topography is smoothly sloping (3%) in a NW direction. The climate is temperate maritime. The soil is 50–100 cm deep and is classified as a dystric cambisol. The vegetation in the tower flux footprint is a mixture of: coniferous species, mainly Douglas fir (*Pseudotsuga menziesii* [Mirb.] Franco) about 40 m high, Norway spruce (*Picea abies* [L.] Karst.) about 32 m high and Silver fir (*Abies alba* Miller) about 32 m high; and deciduous species, mainly beeches (*Fagus sylvatica* L.) about 28 m high. Douglas fir is the main species found in the NE sector (330–90°, North = 0°) while a heterogeneous mixing of beeches (dominant species), Norway Spruce and Silver fir is found in other wind sectors. A more detailed description of this site is given by Aubinet et al. (2001, 2002) and Laitat et al. (1999).

2.2. Instrumentation and BVOC sampling

An ultrasonic anemometer (model SOLENT 1012 R2, Gill Instruments Ltd, Lymington, UK) was placed at a height of 52 m and continuously measured the three wind velocity components at a 20.8 Hz sampling frequency. Ambient air was continuously sampled close to the sonic anemometer through a 60 m-long sampling line with an inner diameter of 6.4 mm, (PFA tubing: Fluortechnik-Wolf) at a flow rate of 9 STP L min^{-1} (Standard Temperature and Pressure corresponding to 1013.25 hPa and 273.15 K). The sampling line was heated to an average of 12 °C above ambient temperature. Part of this air flow (0.1 STP L min^{-1}) was drawn into a gas analyser through a 1.2 m-long heated capillary inlet line (333 K) with an inner diameter of 1 mm. The data streams from the two instruments were logged on a single computer in order to optimise synchronization.

The measurements of relevant meteorological variables were performed at a 0.04 Hz sampling frequency and averaged over half an hour. They included the total and diffuse fraction of photosynthetically active radiation (PPFD, Sunshine sensor type BF3, Delta-T Devices Ltd, Cambridge, UK), air temperature and humidity (RHT2, Delta-T Devices Ltd, Cambridge, UK) at a height of 50 m, atmospheric pressure (MPX4115A, Motorola, Phoenix, USA) and soil temperature (PT100) was measured at 3, 5.5, 9, 26 and 56 cm depths. The sensible heat flux (H), the friction velocity (u^*) and the wind velocity (U) half-hour computations were performed using the sonic anemometer measurements at a height of 52 m.

VOC mixing ratios were measured by a conventional quadrupole-based high-sensitivity Proton Transfer Reaction - Mass Spectrometry instrument (hs-PTR-MS, Ionicon Analytik GmbH, Innsbruck, Austria). Detailed descriptions of the PTR-MS technique are given by Lindinger et al. (1998), de Gouw and Warneke (2007) and Ammann et al. (2004). The instrument 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), where E is the electric field and N the ambient air number density in the flow/drift tube. Ion signals were measured in a cyclic way at 10 mass-to-charge (m/z) ratios in 2009 and 12 in 2010, including m/z 21 ($H_3^{18}O^+$), m/z 69 (protonated isoprene), m/z 81 (monoterpenes fragment) and m/z 137 (protonated monoterpenes). As such, a disjunct time series was produced for the ion intensities at each m/z value. The dwell time for all masses including m/z 21 was 200 ms, ending precisely in a measurement cycle length of 2.212 s in 2009 and 2.852 s in 2010. The ratio of m/z 81 to 137 was monitored to identify the possibility that other compounds might interfere with the monoterpene ion signal. This ratio was observed statistically constant in 2009 and 2010 which implied that no other compounds have interfered with the monoterpene ion signal. During the measurements, the instrumental background was determined every 4 h by sampling BVOC-free air, which involved sending continuously ambient air flow through a continuously heated catalytic converter for 15 min (the last 8 min being used to calculate the mean background values). The sensitivity of the instrument was calibrated for the main target compounds (isoprene, sum of monoterpenes, methanol, acetone and acetaldehyde) every 2 or 3 days using a gravimetrically prepared mixture of these gases in N_2 (Apel-Riemer Environmental, Denver, CO, USA) that contained approximately 500 ppbv isoprene, α-pinene and sabinene and about 1 ppmv methanol, acetaldehyde and acetone, with an accuracy of 5%. The compounds were further diluted (2–12 ppbv range) using a dynamic dilution system. There are more details in Laffineur et al. (2012, 2011).