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Fluxes of biogenic volatile organic compounds above temperate Norway spruce forest of the Czech Republic

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ABSTRACT

Norway spruce (*Picea abies*), the most representative forest species in central and northern Europe, has previously been described as a monoterpene emitter. However, past studies have shown variable emission rates. In order to understand emissions at the ecosystem scale, a technique utilizing proton-transfer-reaction-time-of-flight (PTR-TOF) mass spectrometry coupled with eddy covariance was applied to determine fluxes of volatile organic compounds and CO_2 above a mountainous Norway spruce forest in the Czech Republic during an intensive field campaign in summer. In addition, an Inverse Lagrangian Transport Model was applied to derive fluxes of various monoterpenes using concentrations measured along a vertical canopy profile by wet effluent diffusion denuder. The Model of Emissions of Gases and Aerosols from Nature (MEGAN) was applied using basal emission factors for sun and shade shoots to predict diurnal fluxes and annual monoterpene emission sums for 5 years. The forest showed itself to be a monoterpene emitter up to 2.03 nmol m^{-2} s^{-1}. Isoprene and 2-methyl-3-buten-2-ol (MBO) reached maximum levels during central hours of the day of 1.6 nmol m^{-2} s^{-1}, whereas daily average maximum fluxes were 1.29 nmol m^{-2} s^{-1} and 0.77 nmol m^{-2} s^{-1} for monoterpenes and sum of isoprene and MBO, respectively. The relationship between monoterpene and CO_2 fluxes revealed that as much as 47% of variance in MT emission is predictable from the actual gross primary production of a spruce ecosystem. Modelled MT fluxes agreed with the measured fluxes in terms of diurnal pattern, particularly when basal emission factors 2.72 nmol m^{-2} s^{-1} and 0.55 nmol m^{-2} s^{-1} for sun and shade shoots, respectively, were used. Nevertheless, strong seasonal variability in MT emission was observed. Our results contribute to better understanding emissions of biogenic volatile organic compounds in central Europe.

1. Introduction

Although forests are regarded as global CO_2 sinks, part of the assimilated carbon is re-emitted to the atmosphere as biogenic volatile organic compounds (BVOCs). BVOC emissions exceed anthropogenic emissions by one order of magnitude, and thus they have profound implications for biosphere–atmosphere exchanges (Guenther et al., 1995). BVOCs contribute to ozone formation at sufficient nitrogen oxides concentration and light intensity and to formation of secondary organic aerosol (Chameides et al., 1988; Unger, 2014; Jokinen et al., 2015). Under conditions of land-use changes combined with radiative forcing, their emissions are increased and diversified (Niinemets et al., 2010; Wu et al., 2012). Additionally, climate change might be regarded as increasing BVOC emissions if warming is considered as the major driving factor (IPCC, 2007; Peñuelas and Staudt, 2010; Kleist et al., 2012).

BVOC emissions are driven by such various environmental factors as temperature, light intensity (Fall, 1999), relative humidity (Vallat et al., 2005), ozone concentration (Peñuelas et al., 1999;

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Stokes et al., 2009), and biotic and abiotic stressors (Niinemets et al., 2004). Isoprene and monoterpenes (MTs) are regarded as the most abundant BVOCs emitted by various plant species. Temperature regulates the release of MTs from storage ducts, whereas light is responsible for *de novo* biosynthesis, and especially in the case of α-pinene (Ghirardo et al., 2010).

Norway spruce (*Picea abies* (L.) Karst.) is an economically important and widespread evergreen tree species of the temperate and boreal zone providing important ecosystem services. As of 2013, about 34% of the Czech Republic was covered by forests and Norway spruce represented 50.7% of that tree population. This prevalent tree species emits considerable amounts of reactive trace gases into the atmosphere (Graus et al., 2006). It is considered to be a monoterpene emitter and only a low isoprene emitter (Kesselmeier and Staudt, 1999). Monoterpenes – and particularly α-pinene, β-pinene, limonene, and myrcene – are the most important BVOCs released from resin canals and storage ducts of spruce needles (Bourtsoukidis et al., 2014a, 2014b; Esposito et al., 2016).

BVOC emissions on a global scale are generally poorly understood (Zemankova and Brechler, 2010), except in the case of boreal forests (Tarvainen et al., 2007; Yassaa et al., 2012). Global emissions of MTs from temperate zone forests are estimated as 7.38 and 5.86 Tg yr^{-1} for coniferous and broadleaved species, while MT emissions from tropical trees, which are considered to be the greatest MT emitters, are estimated up to 82.9 Tg yr^{-1} (Guenther et al., 2012). This is given by the large leaf area index of tropical forests, as otherwise both tropical and boreal coniferous species evince similar emission capacity per unit of leaf mass (Kuhn et al., 2002; Ruuskanen et al., 2005). Even less is known about such oxygenated BVOCs as aldehydes and ketones of temperate zone forests, despite the fact that their contribution can reach as much as 24% of the total BVOC emission budget (Guenther et al., 1995).

In various modelling approaches, temperature and light intensity are considered to be the most important drivers of isoprene emission (Staudt and Lhoutellier, 2011), whereas MT emissions of conifers are regarded as only temperature dependent (Guenther et al., 1993). New studies have revealed a partial light dependence, which suggests that models should take into account the light dependency of MT emissions (Ghirardo et al., 2010). Large uncertainties among the models are found due to the large number of BVOCs emitted and the great variability of their basal emission factors (Hewitt and Street, 1992; Simpson et al., 1995; Wiedinmyer et al., 2004; Tarvainen et al., 2007; Bourtsoukidis et al., 2014a). More precise estimates of BVOC emissions are thus needed to capture the changing chemosphere and evaluate emission inventories under current and future climates.

In the present study, BVOC fluxes between a mature Norway spruce forest and the atmosphere were measured using two different approaches: (1) eddy covariance technique coupled with high-frequency proton-transfer-reaction-time-of-flight mass spectrometry (PTR-TOF-MS), and (2) concentration gradient across a vertical canopy profile by cylindrical wet effluent diffusion denuder with subsequent application of an Inverse Lagrangian Transport Model (Raupach, 1989; Nemitz et al., 2000; Karl et al., 2004, 2008; Alves et al., 2016). The Model of Emissions of Gases and Aerosols from Nature (MEGAN) parameterized with the local conditions and the measured basal emission factors were applied to predict MT fluxes for an extended period of time in order to evaluate the effects of environmental conditions on MT emissions. Specifically, we tested two hypotheses: (1) monoterpene emissions from spruce forest are related to an actual photosynthesis rate expressed as gross primary production (GPP), and (2) MEGAN predictions of monoterpene emissions are substantially improved by parameterizing the model using specific basal emission factors for sun and shade needles respectively.

2. Materials and methods

2.1. Site description

The investigated forest stand is located at the Bílý Kříž experimental research site within the Beskydy Mountains in the north-east of the Czech Republic (49° 30′N, 18° 32′E; 875–908 m a.s.l.). This area has a moderately cool (annual mean air temperature 6.6 °C) and humid (annual mean relative air humidity 84.7%) climate with high annual precipitation pattern (mean for years 2009–2014 is 1152 mm). The region is characterized by low nitrogen oxides concentration (NO_x; below 10 parts per billion by volume) and high ozone concentration (O_3; up to 80 parts per billion by volume) during summer months (Zapletal et al., 2011). At present, the experimental research site is a part of various international research networks and infrastructures, including CzeCOS (Czech Carbon Observation System), ICOS (Integrated Carbon Observation System), and AnaEE (Analysis and Experimentation on Ecosystems).

The studied forest stand (99% *P. abies* and 1% *Abies alba*) had been established in 1981 by row planting of 4-year-old Norway spruce seedlings. Mean stand slope is 12.5° and exposure is to the south. In 2012 and 2014, respectively, stand height was 15.2 and 16.7 m, tree density 1268 and 1256 trees ha^{-1}, and hemispherical leaf area index 7.52 and 10.05 m^2 m^{-2}.

2.2. Measurement of microclimatic factors and CO_2 fluxes

Interpretation and modelling of BVOC fluxes were based on such actual microclimatic factors as light intensity, air temperature, relative air humidity, wind velocity and direction, and air pressure. A meteorological mast (36 m tall) placed within the studied stand was equipped with a set of meteorological sensors for air temperature and relative air humidity (EMS33 Rotro, EMS, Brno, Czech Republic), air pressure (PTB110 Barometer, Vaisala, Vantaa, Finland and SPA 511 B5UB, CRESSTO, Roznov pod Radhostem, Czech Republic), precipitation (Precipitation Gauge 386C, Met One Instruments, Grants Pass, OR, USA), intensity of incoming, transmitted and reflected photosynthetically active radiation (EMS12, EMS, Czech Republic), and wind velocity (50.5 Sonic Sensor, Met One Instruments, USA). In addition, air temperature was measured in the middle of canopy height using an RHA1 sensor (Delta-T Devices, Cambridge, UK) and global radiation above the canopy using a pyranometer CM6B (Kipp & Zonen, Delft, Netherlands). Air humidity and wind velocity were measured at 14.28 m above the surface. For details on the instrumentation setup, see Urban et al. (2012). The campaign primarily included clear sky days with only transient cloud covers followed by reduction in global radiation intensity.

Fluxes of CO_2 between the forest stand and atmosphere were measured by eddy covariance method. The eddy covariance system consisted of a Gill HS-50 ultrasonic anemometer (Gill Instruments, Hampshire, UK) and a LI-7200 enclosed-path infrared gas analyser (LI-COR, Lincoln, NE, USA) placed on a micrometeorological mast at 20.5 m above the soil surface. The post-processing of high frequency data (20 Hz) was performed by EddyPro software (LI-COR, USA) according to recent recommendations (Aubinet et al., 2012) and produced half-hourly estimates. This procedure included spike removal and quality check of the raw signals, rotation of wind velocity components into the planar fit coordinate system (Wilczak et al., 2001), and spectral corrections of computed fluxes (Moncrieff et al., 2005). The missing and excluded data, based on quality checking scheme adequate to Mauder et al. (2013), were gap-filled by marginal distribution sampling method according to Reichstein et al. (2005).