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Isoprene and terpenoid emissions from *Abies alba*: Identification and emission rates under ambient conditions

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HIGHLIGHTS

- ► Seasonal variation of BVOC emissions from *Abies alba* trees under ambient conditions in Flanders (Belgium).
- ► Isoprene was the main emitted compound (86–93% of the total BVOC emissions), which was never quantified.
- ► Emission spectrum consisted of 27 compounds including 7 SQT.

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ABSTRACT

In this study, biogenic volatile organic compound (BVOC) emissions from *Abies alba* were studied under ambient conditions in Flanders (Belgium). Emission patterns and rates were investigated from April till November 2010 by using the dynamic branch enclosure technique. The present work revealed that *A. alba* is an isoprene emitter, with isoprene accounting for 86–93% of total BVOC emissions, except during budburst (67%) in May. The emission spectrum of *A. alba* consisted of 27 compounds. Next to isoprene, the main emitted compounds were α-pinene, β-pinene, camphene and limonene. BVOC emissions showed a peak in June after development of the young needles, followed by a constant emission during summer months and September and a decrease in October. In all the samples isoprene was the most abundant compound with standardized emission rates between 27 $\mu g\ g_{(dw)}^{-1}\ h^{-1}$ in June and 4.6 $\mu g\ g_{(dw)}^{-1}\ h^{-1}$ in October, while the total standardized terpenoid emission rates ranged from 2.85 $\mu g\ g_{(dw)}^{-1}\ h^{-1}$ in June to 0.26 $\mu g\ g_{(dw)}^{-1}\ h^{-1}$ in October. The obtained average β coefficients according to the temperature dependent algorithm of Guenther et al. (1993) during April–June, July, August and September–October were as follows: for terpenoids 0.12 ± 0.03, 0.11 ± 0.05, 0.12 ± 0.04, $0.24 \pm 0.01\ K^{-1}$ and sesquiterpenes (SQTs) 0.09 ± 0.02, 0.11 ± 0.01, 0.10 ± 0.05, $0\ K^{-1}$, respectively. Overall, isoprene detected in this study was never quantified in previous studies on *A. alba* and this finding could have a significant impact on the regional BVOCs budget. Therefore, the result of this study is very important for modeling and local air quality.

1. Introduction

Biogenic volatile organic compounds (BVOCs) are a heterogeneous group of compounds that includes isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$) and oxygenated compounds such as methanol, acetone, 6-methyl-5-hepten-2-one, linalool (Atkinson and Arey, 2003). BVOC emissions have been identified from trees, grasses, crops, and other plants (Kesselmeier and Staudt, 1999). BVOCs such as isoprene and monoterpenes are reactive [interact with hydroxyl radicals ($OH^\bullet$), nitrate radicals ($NO_3^\bullet$) and ozone (O_3)] and oxidation of these compounds results in production of carbon monoxide (CO) and carbon dioxide (CO_2) (Andreae and Crutzen, 1997; Guenther, 2002). BVOCs contribute to the formation of O_3 and secondary organic aerosols (SOA) and thus can play important roles in the Earth global system, providing a connection between biosphere and atmosphere (Arneth et al., 2008; Laothawornkikul et al., 2009).

The BVOC budget at regional scale is crucial for proper modeling of their global emissions and prediction of air quality and climatic changes. Most of the reported mathematical models include the short-term responses to temperature and light for many plants/

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compounds (Tingey et al., 1980; Guenther et al., 1991; Schuh et al., 1997; Staudt and Bertin, 1998) to simulate the temporal variation of emissions over a year. Guenther (1997) and Staudt et al. (2000) reported that seasonal effects may have the greatest impact on emissions, and hence should be considered as relevant to long-term predictions. Since the reliability of atmospheric models depends on the quality of the input data, development of BVOC inventories requires an extensive regional analysis and field studies.

Studies on BVOC emission are reported under controlled laboratory conditions and information on seasonal changes in emission pattern and rate for many common tree species (*Abies alba*, *Fraxinus excelsior*, and *Larix decidua*) under natural conditions are rather limited. Moreover, BVOCs emission analysis under natural conditions is affected by several factors including biotic and abiotic stress and phenology (Joó et al., 2010; Pokorska et al., in press). Therefore, in many regions BVOC emissions remain uncertain and the estimated values of isoprene emissions in the European inventory can vary by a factor 5 (Simpson et al., 1995).

A. alba, a coniferous evergreen tree (commonly known as silver fir, genus *Abies* and family Pinaceae), is one of the most important trees from an economic and ecological point of view, growing naturally in Europe. *A. alba* trees are distributed in mountainous regions of eastern, western and central Europe (Wolf, 2003). A few studies have been reported on *A. alba* emission characterization either in laboratory experiments (Isidorov et al., 1985; Isidorov, 1992; Dormont et al., 1998) or in a short 5-day measurement campaign carried out under natural conditions (Moukhtar et al., 2006). Therefore there is a lack of seasonal BVOC emission data of this abundant tree species.

Overall, there are very few references for emission rates measured under natural conditions in Europe. In this context, the aim of the present study is to characterize BVOC emission from *A. alba* under ambient conditions. The investigations presented in this paper focus on how environmental parameters influence BVOC emission from *A. alba* over seasons in Flanders (Belgium).

2. Materials and methods

2.1. Branch enclosure and analytical system

This study was carried out on *A. alba* trees grown at the Vielsalm forest (Belgian Ardennes forest 50°18′18.20″N, 5°59′53.15″E, altitude: 450 m). Three healthy *A. alba* trees (AA1, AA2, and AA3) with varying height (1–1.5 m) were carefully dug out with the soil surrounding the roots, placed in pots and transported to the campus of the Faculty of Bioscience Engineering Ghent University at the beginning of March 2010.

Measurements of BVOC emissions with the dynamic branch enclosure system were performed under ambient conditions at the campus of the Faculty of Bioscience Engineering Ghent University (51°3′13″N, 3°42′22″E). The sampling campaign started before needle development (27th April 2010) and lasted till 29th of October 2010. In total 119 (AA1 $n = 77$, AA2 $n = 21$, AA3 $n = 21$) samples were collected through the entire experimental period. A branch of the AA1 tree was placed in the cuvette in April and it remained there till July in order to follow changes in BVOC emissions during budburst and needle development. From July onwards samples of AA1 were collected on a monthly basis. Additionally AA2 and AA3 trees were sampled simultaneously in August and October. The same branches of each tree were sampled through the whole measurement period. Needle dry weight was determined at the end of each experiment.

The dynamic branch enclosure system and analytical methodology has been described in detail elsewhere (Pokorska et al., in press). Briefly, the set-up consisted of an air supply system and 3 enclosures equipped with inlet and outlet ports. Cuvettes (volume 21 L each) were flushed with VOC and ozone free air at flow rates of 6–8 L min^{-1}. All parts of the set-up were made of perfluoroalkoxy Teflon (PFA) to prevent losses of compound by sorption on the material. Additionally, Teflon ventilators were mounted in the cuvettes to ensure proper mixing of emitted BVOCs and the incoming air. The climate conditions were characterized by continuous measurements of photosynthetic photon flux density (PPFD) (sensor Li-190SA, Li-Cor, USA), air temperature inside the cuvette (thermistor type 10k, NTC, Omega, NL) and relative humidity (sensor type HIH-3610, Honeywell, NJ, USA). In the present study only ambient air temperature was monitored. However, ambient and enclosure temperatures are expected to be in reasonable agreement (±3 °C difference) as reported by Joó et al. (2011). Before enclosure of new branches, the cuvettes were cleaned and blank samples were taken from the empty cuvettes to ensure that there was no contamination from previously measured branches. The samples collection took place 24 h after branch enclosure to avoid stress-induced BVOC emission.

Samples were collected on glass sorbent tubes, filled with preconditioned Tenax TA and Carbotrap (Markes International, Llantrisant, UK), by pumping air from the enclosure at a constant flow of 100 mL min^{-1}. Tubes were also pre-loaded with an internal standard [$^2H_8$] toluene (Tol-d_8) and n-alkanes for the determination of linear retention indices. Headspace of Tol-d_8 and n-alkanes (500 mL each) was loaded always into conditioned absorbent tubes before sampling. Description of preparation of the Tol-d_8 headspace as a closed two-phase system (CTS) can be found in Demeestere et al. (2008).

Afterwards, the adsorption tubes were closed with Swagelok fitting, stored at room temperature and analyzed within 24 h. Samples were desorbed using a thermal desorber and autosampler (Markes International, Llantrisant, UK) and then analyzed by a GC Trace 2000 gas chromatograph (ThermoFinnigan, Milan, Italy) coupled with a Trace DSQ Quadrupole mass spectrometer (ThermoFinnigan, Austin, TX, USA). Compounds were separated on a VF-1 column (Varian, Sint-Katelijne Waver, Belgium; 100% polydimethylsiloxane (PDMS), length 30 m, inner diameter 0.25 mm, film thickness 1 μm). Each sample was scanned in two alternating modes: the total ion current (TIC) mode with a mass range m/z of 45–222 and the selected ion monitoring (SIM) mode, where m/z 53, 67, 68 were selected for hemiterpenoids (0–10 min), m/z 98, 100 for Tol-d_8 (10–13 min), m/z 91, 93, 121 for monoterpenes (MTs) (13–31), m/z 69, 93, 204 for sesquiterpenes (SQTs) (31–43 min). Peaks were quantified if they were above the limit of detection (LOD, 3:1 signal to noise) in the TIC mode and above the limit of quantification (LOQ, 10:1 signal to noise) in the SIM mode. Identification of the compounds was based on reference mass spectra and retention indices obtained by injection of standards. If standards were not available, identification was made by comparison of obtained spectra and retention indices with the NIST library (National Institute of Standards and Technology library), the Mass Finder database (Mass Finder 4software, Hamburg, Germany) and literature data. Calibration of GC–MS was performed monthly by using a gravimetrically prepared mixture of isoprene (0.515 ppm_v), α-pinene (0.496 ppm_v), β-pinene (0.501 ppm_v), sabinene (0.499 ppm_v), limonene (0.486 ppm_v), linalool (0.473 ppm_v) and (Z)-3-hexenyl acetate (0.499 ppm_v) in nitrogen (Apel – Riemer Inc., Denver, CO, USA), with certified accuracy of 5%. The response factor of sabinene was used for quantification of the compounds which were not present in the calibration mixture. Due to limitation of the analytical system peaks of myrcene and β-pinene were not well separated and reliable quantification of these two compounds could not be