**Atmospheric
Chemistry
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Discussions**

Seasonal variation in vertical volatile compounds air concentrations within a remote hemiboreal mixed forest

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Abstract

The vertical distribution of ambient biogenic volatile organic compounds (BVOC) concentrations within a hemiboreal forest canopy was investigated over a period of one year. Variability in temporal and spatial isoprene concentrations can be mainly explained by biogenic emissions from deciduous trees, ranging from 0.1 to 7.5 μg m^{-3}. Monoterpene concentrations exceeded isoprene largely and ranged from 0.01 to 140 μg m^{-3} and during winter time anthropogenic contributions are likely. Variation in monoterpene concentrations found to be largest right above the ground and the vertical profile suggest a weak mixing leading to terpene accumulation in the lower canopy. Exceptionally high values were recorded during a heat wave in July 2010 with very high midday temperatures above 30 °C for several weeks. During summer months, monoterpene exceeded isoprene concentrations 6-fold and during winter 12-fold. The relative contribution of diverse monoterpene species to the ambient concentrations revealed a dominance of α-pinene in the lower and of limonene in the upper part of the canopy, both accounting for up to 70 % of the total monoterpene concentration during summer months. The main contributing monoterpene during wintertime was Δ^3-carene accounting for 60 % of total monoterpene concentration in January. Possible biogenic monoterpene sources beside the foliage are the leaf litter, the soil and also resins exuding from stems. In comparison, the hemiboreal mixed forest canopy showed similar isoprene but higher monoterpene concentrations than the boreal forest and lower isoprene but substantially higher monoterpene concentrations than the temperate mixed forest canopies. These results have major implications for simulating air chemistry and secondary organic aerosol formation within and above hemiboreal forest canopies.

1 Introduction

Emissions of biogenic hydrocarbons from forest ecosystems are a dominant source of reduced organic gases to the atmosphere. They even exceed emissions of hydrocarbons by anthropogenic pollution and biomass burning. Biogenic emissions play important roles in determining the global, regional, and local atmospheric chemistry which, in turn, feeds back to the ecosystem (Arneth et al., 2010; Kulmala et al., 2004).

Losses of instantaneously emitted hydrocarbons such as terpenes due to oxidation processes throughout the canopy height have been reported by several studies (Holzinger et al., 2005; Fuentes et al., 2007; Stroud et al., 2005). Especially if the canopy height and structure together with atmospheric turbulence is such that the residence time of air parcels within the canopy are comparable or greater than the lifetimes of BVOCs, chemical losses and deposition within the canopy lead to reduced total surface emissions (Fuentes et al., 2007; Karl et al., 2004; Strong et al., 2004). Effects of ozone, nitrogen oxides (NO_x) and hydroxyl radical (OH) on the vertical distribution of BVOCs or vice-versa have been also assessed by means of 1-D canopy chemistry models including atmospheric transport terms (Forkel et al., 2006; Fuentes et al., 2007; Karl et al., 2004; Stroud et al., 2005; Strong et al., 2004). These studies mostly conclude that the discrepancy between upscaled leaf level BVOC emission fluxes and canopy scale flux measurements are due to the within canopy chemistry that lead to a reduction in total surface BVOC emission to the boundary layer. Monoterpene uptake by leaves of deciduous tree species under high ambient concentrations occurs and leads to altered temporal behavior of total monoterpene fluxes. Such processes have been described by Copolovici et al. (2005) and Noe et al. (2008).

Seasonal variations in isoprene and monoterpene emissions have been widely reported for a large variety of ecosystems and tree species (Holzinger et al., 2006; Hakola et al., 2003, 2009; Sabillón and Cremades, 2001; Mayrhofer et al., 2005) and also entered into emission models on various scales (Schurgers et al., 2009; Guenther et al., 2006). In some cases only total monoterpene fluxes have been taken into account

and α-pinene is commonly used as a proxy to represent all monoterpenes. This is in contrast to the finding that monoterpenes have quite different atmospheric lifetimes (Atkinson et al., 1990; Atkinson, 2000; Lyubovtseva et al., 2005) suggesting differences in their chemical degradation and impact on subsequent processes such as secondary organic aerosol (SOA) formation (Ng et al., 2008; Kanakidou et al., 2005; Spracklen et al., 2008).

Forest trees are exposed to a huge amount of biotic and abiotic stresses and environmental factors that lead to very heterogenous emission patterns of biogenic hydrocarbons (Niinemets, 2010a). Inclusion of process-based approaches, addressing such factors on larger scale emission fluxes of biogenic hydrocarbons have been reviewed recently (Niinemets et al., 2010b; Arneth et al., 2008; Arneth and Niinemets, 2010; Niinemets, 2010b). The findings of Stroud et al. (2005) and Karl et al. (2004) already led to an empirical term for the escape efficiency of biogenic hydrocarbons from forest canopies into the boundary layer. That escape efficiency has been included to the MEGAN framework (Guenther et al., 2006) to allow to scale biogenic hydrocarbon emissions to regional or global levels.

Estonia is located at the transition zone between the boreal and temperate biomes which characterizes the location of hemiboreal, mostly mixed, forests. Nilsson (1997) estimates the width of that transition zone over Eurasia to span at least over 600 km (Sweden) and even wider in Siberia (Russia). Given predictions on species diversity and their change under future climate in Scandinavia (Sætersdal et al., 1998) and the likely climatic impact on northern ecosystems (Intergovernmental Panel on Climate Change, 2007), it seems likely that the hemiboreal transition zone will move and enlarge to north. Until now only few studies have been pointed to the atmosphere-biosphere relations within that zone. The aim of our study was to give (1) an overview on the ambient isoprene and monoterpene concentrations within a remote hemiboreal mixed forest canopy to asses (2) the seasonal change and reveal variations in ambient concentrations due to the changes in environment and to study (3) the spatial heterogeneity of isoprene and monoterpene ambient concentrations within the canopy.

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2 Materials and methods

2.1 Site description

The vertical VOC profiles were measured at a 20 m high tower located in the Järvselja Experimental Forest in southeast Estonia (58°25′ N, 27°46′ E). The site is situated in the hemiboreal forest zone with a moderately cool and moist climate and is described in more detail by Noe et al. (2010). It is characterized as a remote site. These transition zones spreading between the boreal and temperate climate zones are populated by conifer dominated mixed forests.

The measurement site is dominated by Norway spruce (*Picea abies* (L.) Karst.) and as co-dominant species Silver Birch (*Betula pendula* Roth.) and Black Alder (*Alnus glutinosa* L.) in the upper canopy layer varying between 16–20 m. The presence of a suppressed tree layer with a mean height between 6–7 m is of particularly importance as it affects turbulent air flows within the stand. The soil is covered by a dense and rather species rich layer of ground vegetation and a moss layer that consists of several species. The site has a lowland character and is influenced by a high groundwater table and water logging due to the vicinity of Lake Peipsi. Especially in humid spots we found *Sphagnum* species which are typical for peat bogs.

The mean annual temperature varies between 4–6 °C and the annual precipitation between 500–750 mm, about 40–80 mm of the annual precipitation is snow. The length of the growing season (daily air temperature above 5 °C) averages between 170–180 days.

2.2 VOC sampling

We conducted the sampling of VOC from ambient air on 6 heights (0, 4, 8, 12, 16, and 20 m above ground) over a year starting in October 2009 until September 2010 (Table 1). The days of sampling have been chosen such that we obtained samples in each season of the year at high air pressure and clear sky.

The samples were directly drawn into multibed stainless steel cartridges (10.5 cm length, 3 mm inner diameter, Supelco, Bellefonte, PA, USA) filled with Carbotrap C 20/40 mesh (0.2 g), Carbopack C 40/60 mesh (0.1 g) and Carbotrap X 20/40 mesh (0.1 g) adsorbents (Supelco). We did not remove the ozone from the sample air stream as that would be a change in the chemical composition of air during the sampling. Further more it was shown that the adsorbent material used has 100 % recovery for BVOC (Calogirou et al., 1996; Ciccioli et al., 1984).

We used a total of three constant flow air sample pumps (1003-SKC, SKC Inc., Huston, TX, USA) and one multi-sample constant flow air sample pump (224-PCXR8, SKC Inc., Huston, TX, USA) that allows to draw four samples at the same time. With this setup we were able to sample a total of at least three repetitions on each height within a time frame of 2–2.5 h around midday local winter time (UTC + 2). Each sampling took 30 min with a flow of 200 ml min^{-1} which concentrated a total of 6 l of ambient air on the adsorbent. The samples were stored and cooled (+5 °C) until analysis which took place within 4 to 6 h after sampling.

2.3 Resin sampling

For comparison with the volatile components found in the air space around tree trunks we took three samples of spruce resin from the stems of the trees surrounding the tower. The samples were taken at about 1 m heights on the stem of spruce trees at places that were exuding resin. The resin was picked using a small spruce stick and transferred into 8 ml glass vials for transport and subsequent analysis.

2.4 VOC analysis

Adsorbent cartridges were analyzed with a combined Shimadzu TD20 automated cartridge desorber and Shimadzu 2010 Plus GC-MS instrument (Shimadzu Corporation, Kyoto, Japan) described previously (Copolovici et al., 2009; Toome et al., 2010).

For the analysis of the resin samples, 0.2 g resin are dissolved in 2 ml hexane and extracted over 24 h at 4 °C. The preparations were shaken at 4 °C for 30 min and then centrifuged at 10 000 g for 5 min. The supernatant was then filtered through two layers of no. 1 filter paper (Whatman, Kent, UK). Determination of the monoterpenes of the resin was achieved by GC-MS (Shimadzu 2010 Plus GC-MS, Shimadzu Corporation, Kyoto, Japan) and equipped with a Shimadzu AOC20 autoinjector/autosampler.

Separation of different compounds was achieved in a ZB-5MS capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness, Zebron, Phenomenex, Torrance, CA, USA). Injector temperature was set at 215 °C. Initial oven temperature was set at 40 °C, held for 1 min; ramped at 5 °C min^{-1} up to 200 °C, held for 1 min; ramped at 10 °C min^{-1} up to 220 °C and held for 5 min. Helium (purity 99.9999 %, Elmer Messer Gaas AS, Tallinn, Estonia) was employed as carrier gas with a constant flow of 0.74 ml min^{-1}. The mass spectrometer was operated in electron-impact mode (EI) at 70 eV, in the scan range m/z 30–400, the transfer line temperature was set at 240 °C and ion-source temperature at 150 °C. Compounds were identified by use of the NIST spectral library and based on retention time identity with the authentic standard (GC purity, Sigma-Aldrich, St. Louis, MO, USA). The absolute concentrations of isoprene, monoterpenes and LOX products were calculated based on an external authentic standard consisting of known amount of VOCs.

2.5 Auxiliary measurements

Beside the main task of assessing vertical VOC profiles throughout the canopy and over the seasons, we measured, predominantly under summer conditions, also ambient temperature, light and CO_2 profiles throughout the canopy.

Temperature measurements have been conducted using a thermocouple sensor that was connected to a thermocouple reader (Comark KM330, Comark Instruments, Hitchin, Hertfordshire, UK). When temperature was measured, the sensor was placed beside the sampling pump and during the sampling time, three to four values of temperature were recorded.

Quantum flux density (PPFD) was measured with a LI-190SA quantum sensor (LiCor, Lincoln, NE, USA). On each height, PPFD was measured in shade conditions and in full sunlight, if available. At least 5 measurements were taken at different locations near the sampling pump and the data averaged.

To assess the ambient CO_2 mixing ratios throughout the canopy, a closed path infrared gas analyzer (IRGA) (LI-7000, Li-Cor, Lincoln, NE, USA) was used. Sample air was drawn from each height by Teflon pipes passing a filter (Acro50, Gelman, Ann Arbor, MI, USA) and the IRGA. An air flow of $10 \, \mathrm{l\,min^{-1}}$ was provided by a vacuum pump (Samos SB 0080 D, Busch Vakuumteknik Oy, Vantaa, Finland).

Horizontal wind speed was measured with two 3-D sonic anemometers (CSAT3, Campbell Scientific, 168 Logan, UT, USA; Metek USA-1, Metek GmbH, Elmshorn, Germany) which have been installed on top of the tower at a height of 20 m above ground and on a mast at a height of 2 m above forest floor for continuous eddy covariance measurements at the site.

3 Results

3.1 Environmental factors

Terpene concentrations in ambient air rely on the emissions from plants as sources and on the chemical composition and oxidative state of the atmosphere determining the sink defined by chemical reactions. Figure 1 shows an example during summer of key environmental drivers that affect both, the source and the sink of terpenes in the atmosphere. The temperature showed a typical pattern for the mid of a clear and sunny day with higher temperatures on top of the canopy and lower ones within the forest. An interesting effect was the outcome, that the variation within that parameter is larger on top of the canopy and directly above the forest floor. The light gradient showed the expected picture that the highest radiative input into the system is at the top of the canopy, were most leaves and needles are located and quickly decreases

within the canopy. Below 8 m height PPFD remain below 100 µmol m^{-2} s^{-1}. Between 12 m to 16 m we found the largest variation of the radiative energy while at the top of the canopy the variation is again small. The carbon dioxide (CO_2) gradient with concentrations at lower levels increasing well above ambient air concentrations is an
5   indicator for reduced mixing of air during summer months, as is indicated also by the variation in horizontal wind speed (Fig. 2)

3.2 BVOC overview

We found a variety of reactive VOC species in the ambient air measured throughout the canopy. The monoterpenes α-pinene, Δ^3-carene, and limonene dominated the
10   ambient concentrations (Figs. 3 and 5) and further β-pinene, camphene and α-thujene were detected. From the shorter chained hydrocarbons, isoprene was detected as well as 1-hexanol and (Z)-3-hexenol. The latter both are likely originated from the plants lipoxygenase (LOX) pathway and typically indicate plant responses to environmental stress factors. During the warm summer months, the trees are likely to face several
15   stresses such as heat, drought and high light (Niinemets, 2010a; Turtola et al., 2003). During June, July and August 2010 we also detected the sesquiterpenes γ-muurolene, α-longifolene, β-caryophyllene, copaene, α-cedrene, and (E,E)-α-farnesene in ambient air with their highest abundance in the upper canopy.

3.3 Seasonal and spatial variation

20   Isoprene and monoterpenes showed a large variability over the whole year (Fig. 3, Supplement Table S1 and S2). The mean values of isoprene varied between 0.1 µg m^{-3} and 7.5 µg m^{-3} with lowest values in April 2010 and highest in July 2010. Mean values of the LOX pathway compounds varied substantially between 0.03 µg m^{-3} and 3.4 µg m^{-3} with highest values exclusively in July 2010 and on the topmost level of
25   the canopy. The mean values of monoterpenes showed the largest variability spanning over five orders of magnitude starting below 0.01 µg m^{-3} and reaching nearly

$100\,\mu g\,m^{-3}$. Highest values were found in July 2010 under exceptionally hot conditions (Table 1 and Fig. 3) reaching $140\,\mu g\,m^{-3}$.

The vertical profiles of isoprene and monoterpenes are presented in the Figs. 3 and 4. For isoprene, we can clearly distinct between the summer months (June to August) and the rest of the year. Comparing the height profile for each month, there was no clear pattern visible over the year (Fig. 3). While in June the highest concentrations was found on the topmost level of the canopy , the profile has changed considerably in August with higher concentrations found inside the canopy. In the case of total monoterpene concentrations, the situation is different. Excluding the exceptionally hot periods, the monoterpenes showed higher concentrations at 0 m and 4 m height over the whole year. Only during July 2010, when a long and exceptional hot period had occurred, the ambient monoterpene concentrations were dramatically increased at 16 m and 20 m height. The same, but much less prominent pattern was seen in August 2010, when the concentrations of monoterpenes were slightly larger on 20 m height than below (Fig. 3).

3.4 Whole year canopy profile

A more general pattern was obtained by combing the measurements per height over the whole year. Figure 4 shows the variation of isoprene and total monoterpene concentrations profiles found. Isoprene median concentrations were found to range between $0.33\,\mu g\,m^{-3}$ and $0.56\,\mu g\,m^{-3}$. The outliers were caused by the measurements in July 2010 and the largest variation was found at 16 m height where the dynamics of the environmental drivers was largest. The monoterpene concentrations were found maximal in the forest understory between soil level and a height of 4 m. Here as well, the outliers came from the measurements in July under high temperatures. The median monoterpene concentrations decreased from $8\,\mu g\,m^{-3}$ at 0 m to $2\,\mu g\,m^{-3}$ at 20 m height and the largest variability over the year was found at 0 m and 16 m (Fig. 4).

3.5 Relative contribution by monoterpene species

To assess changes in the contribution of several monoterpene species emitted we normalized the total monoterpene concentration to one and expressed each monoterpene by its relative contribution (Fig. 5). These relative contributions showed as well a gradient over the canopy. While near to the forest floor, α-pinene was the most abundant species, we found limonene dominating on top of the canopy for most times of the year. Δ^3-carene showed the smallest fractional contribution to the total monoterpene concentrations at 0 m for the most times measured and its contribution was growing to top of of the canopy. Overall, the heterogeneity and variability was larger at the top of the canopy than at the forest floor.

4 Discussions

In general, the values we present here fit into the picture of the reported ambient isoprene and monoterpene concentrations. Such ambient concentrations range from 2 to 5 μg m^{-3} for isoprene and and 10 to 18 μg m^{-3} for monoterpenes in boreal forest ecosystems (Hakola et al., 2000; Rinne et al., 2000; Räisänen et al., 2009). Further ambient terpene concentrations were reported for Greece (Harrison et al., 2001), the Amazon (Rinne et al., 2002), Duke Forest and Oak Ridge in USA (Stroud et al., 2005; Fuentes et al., 2007), where Oak Ridge employed the highest isoprene mixing ratios among the sites noted here.

During spring and summer, our measurements resulted in isoprene values that ranged from 1 to 7 μg m^{-3} and the monoterpene concentrations varied in the same time between 10 and 40 μg m^{-3} if the extreme values measured in July 2010 were excluded. Given reported maximal values for boreal forests (Räisänen et al., 2008, 2009; Eerdekens et al., 2009) the numbers reported here are slightly higher. Hakola et al. (2009) reported as well yearly and monthly averages of monoterpene concentrations which are reflected by our values, if taken out the exceptional July measurements.

Overall the hemiboreal forest ecosystem employ slightly larger ambient monoterpene concentrations than the boreal forest and clearly larger than temperate forests where less monoterpene emitting species are present. For isoprene, the hemiboreal forest show slightly larger ambient concentrations than the boreal forest but is clearly below the temperate forest concentrations.

4.1 Seasonal variation of the ambient terpene concentrations

The seasonal variation in isoprene and monoterpene concentrations is, as expected, rather big. Wintertime values reflect the lowest and the summertime values the highest biogenic activity. Our measurements support the idea that throughout the year the relative contribution of different biogenic sources to ambient terpene concentrations is changing substantially.

The concentrations for isoprene in winter, spring and autumn remained quite similar even though, the temperatures, state of the surface (snow cover in winter, flood in spring) and the physiological conditions of contributing tree species changed substantially during those periods. The deciduous trees lost their leaves and also reached bud burst and developed new foliage causing changes in the light and temperature environment within the forest canopy. However, such dramatic environmental changes, impacting on the biogenic sources and the chemical sinks, did not lead to substantial changes in ambient isoprene concentrations during the most time of the year. Interestingly, the isoprene concentrations during January were larger than in October and April. That might be due to a low chemical sink and possible anthropogenic influences, that have been reported (Reimann et al., 2000). Such anthropogenic sources are mainly the combustion and evaporation of fossil fuels as well as biomass burning (Reimann et al., 2000; Theloke and Friedrich, 2007; Cai and Xie, 2009).

In contrast, the summer months (June, July and August) showed a very large heterogeneity in the isoprene concentrations increasing up to 7-fold as compared to the rest of the year. That pattern was found consistently over the vertical gradient measured

and suggests that the activity of the biogenic sources is largely increased throughout the canopy and follows basically an asymmetric seasonal variation (Niinemets et al., 2010a).

The ambient monoterpene concentrations followed as well the asymmetric seasonal pattern and employed the highest concentrations during summer. However, that pattern was not consistent over the spatial distribution within the canopy and will be discussed below. Monoterpenes dominated the terpene trace gas concentrations in the forest air over the whole year. When calculating the mean isoprene and monoterpene concentrations during the summer months, monoterpene concentration exceeded the isoprene concentration 6-fold. During winter, spring and autumn, the monoterpene concentration dominated even more and exceeded the isoprene concentration 12-fold.

Given the tree species distribution at the measurement site (Noe et al., 2010), the loss of the leaves from the fraction of deciduous trees and, by that a change in sources of both, monoterpenes and isoprene, led to a change of the ambient terpene composition. While the monoterpene concentration remained dominated by biogenic sources there might be anthropogenic contributions to isoprene during winter time. We can not proof that with our data and that was not the intention to do so but investigating the source location is a future task to better understand the role of the annual changes of the hemiboreal ecosystems and their impact on the atmospheric state and feedbacks thereof.

4.2 Vertical variation through the canopy

Light availability discriminates the most the activity of the biogenic sources and the chemical sinks within the forest canopy. Up to today, information on vertical variation of BVOC is scarce (Fuentes et al., 2007; Eerdekens et al., 2009). Recent studies showed (Noe et al., 2010; Fuentes et al., 2007; Eerdekens et al., 2009) that reactive trace gas concentrations are substantially smaller within the canopy under shade conditions than above the canopy in sunlight. Furthermore, Eerdekens et al. (2009) reported larger terpene concentrations at night time indicating the loss of activity in the chemical

sink when there is no or low light. While our measured isoprene concentration did not change very much, the total monoterpene concentration was increased by a factor of two or three, depending on the height in the canopy. This indicates, that the change in the oxidative state due to lack of light may influence substantially the accumulation of monoterpenes within the canopy.

Another factor that may impact, at least during the summer months, is the rather dense canopy that leads to a weak mixing of the lower forest air layers (Fig. 2). Beside trees, also the soil is a source of monoterpenes and high concentrations have been reported for soil under *Pinus sylvestris* L., *Betula pendula* L. and *Picea abies* L. (Isidorov et al., 2010; Aaltonen et al., 2011). Soil airspace concentrations have been reported to be about a factor of 1000 larger than in ambient air (Smolander et al., 2006) and a contribution of monoterpenes emitted from soil to the concentration in forest air is a likely process.

The general pattern of the vertical terpene concentration is seen by the yearly median values. Isoprene concentrations remained almost constant over the canopy height and employed the largest variations at 16 m height. There is the main part of photosynthesizing foliage located and the highest source activity. At 20 m in full sunlight, the chemical sink and the mixing is stronger and thus the possible isoprene concentrations are smaller.

The median monoterpene concentration tends to be highest at the forest floor until 4 m height and then decreases by a factor of four until the top of the canopy. Largest variations were found at the forest floor and at 16 m height. This can be seen as an indication that soil and litter is an important monoterpene source near the forest floor and the biogenic source is strongest at 16 m where the largest amount of leaves are located in summer. At 20 m, again the stronger oxidation processes and mixing should lead to lower ambient concentrations.

4.3 Temporal and spatial variation in the relative monoterpene contribution

The main contributing monoterpenes changed over time and space within the forest canopy. The dominant compound in the lower canopy was α-pinene while on the top of the canopy limonene took that role. An exception to that pattern was the Δ^3-carene contribution which was dominant in January on all heights. A possible explanation is the logging activity which took place in winter. We know that Δ^3-carene is the main compound emitted from *P. abies* (Noe et al., 2010) at our site and it shared up to 14 % of the spruce resin monoterpene content. Because of that, Δ^3-carene emissions from freshly cut and stored logs in the surrounding are a likely source.

Taking the lifetime and reaction rate constants of α-pinene and limonene into account (Atkinson, 2000), the temporal and spatial relative contribution pattern give some indications on the change in the activity in the biogenic sources. Above the canopy the chemical loss of limonene should be larger than for α-pinene. As it was found to be the most abundant monoterpene in ambient air at 20 m, there has to be a large source activity. One explanation during the summer months might be an increased limonene emission flux under heat stress as reported for *Pinus sylvestris* and *Picea abies* (Turtola et al., 2003). However, a recent study did not reveal the same pattern in leaf level monoterpene fluxes during summer (Noe et al., 2010). That indicates that a simple link between leaf level fluxes and ambient concentrations in a system with multiple influencing factors might hold only temporarily.

The monoterpene concentrations inside the forest, especially near the forest floor, showed a clear contribution pattern. This pattern was present even in early spring with snow cover and flooding after the snow melted away. Comparing the measurement of the monoterpene contribution in ambient air to soil and litter fluxes (Fig. 5 and Table 2) the fractions we found for α-pinene and limonene resemble most closely the soil efflux found in the boreal forest (Aaltonen et al., 2011). Even though soil and litter efflux were found to be slow as compared to the leaf fluxes (Noe et al., 2010) a weak mixing and low windspeed (Fig. 2) during summer with a very dense foliage on top could lead to monoterpene accumulation inside the canopy.

Yet, monoterpene contributions from soil or litter are scarcely investigated. Possible sources are soil microbes (Ramirez et al., 2010) and the litter (Gray et al., 2010; Isidorov et al., 2010). Hayward et al. (2001) reported also differences in VOC fluxes according to the depth of the soil. However, the comparison with litter and soil flux samples (Table 2) suggests that there is a large variability in litter and soil monoterpene fluxes. In our case, the spruce resin is one potential source contributing to the ambient concentrations measured from early spring to autumn. As resin is located within the litter and the trunks, there is a substantial spatial cover within the forest canopy for such monoterpene contributions to the ambient concentration.

5   Conclusions

We found clear seasonal and spatial pattern of isoprene and monoterpene ambient concentrations within the forest canopy. While the variation in the isoprene concentration can mainly be explained by the biogenic emission from deciduous trees, the monoterpene concentrations showed the largest values and variations above the forest floor.

During summertime, very large stress related emissions from the biogenic sources led to large ambient concentrations despite of the also high oxidation sink for terpenes. Especially monoterpene concentrations were the dominant terpenes in forest canopy air.

The relative contribution of monoterpenes let us propose several possible sources within the canopy. The main sources during the growing season are the foliage and under high temperature the stress related emissions can temporarily dominate the source capacity. The forest floor (soil and litter) is a strong source, especially for α-pinene throughout the year and resins may contribute as well in that temporal range. The measurement in January was dominated by Δ^3-carene and anthropogenic sources play a role during wintertime.

We can conclude that the lower canopy is weakly mixed and rather stable during spring and summer leading to at least two clearly distinct layers within the canopy. Oxidative degradation processes inside the canopy may play a more prominent role during that time. In autumn and winter the patterns resemble more to the situation of the boreal forest with coniferous trees as main contributors of biogenic hydrocarbons and a rather open canopy structure allowing stronger mixing.

Predictions of BVOC fluxes by means of vegetation maps that grade the hemiboreal area as temperate mixed forests are likely to overestimate the isoprene and underestimate the monoterpene fluxes to the boundary layer.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/14607/2011/ acpd-11-14607-2011-supplement.pdf.

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Table 1. Overview of the meteorological conditions on the days when VOC vertical profile sampling was conducted. All values are reported as hourly averages during the time of measurements and refer to the top of the measurement tower at 20 m. The type of measurement conducted refers as follows v = volatile sampling, t = temperature measured on all heights, l = light measured on all heights. The sampling was in all cases conducted under clear sky conditions.

measurement date	type	wind direction	wind speed (m s^{-1})	temperature (°C)	air pressure (hPa)
Oct 2009	v	209°	3.7	7.8	1022.7
Jan 2010	v	56°	1.9	−19.4	1042.7
Apr 2010	v	285°	1.1	8.2	1021.1
Mai 2010	v	61°	3	24.5	1012.5
Jun 2010	v	270°	1.5	24.3	1021.1
Jul 2010	v, l	167°	5.7	31.2	1006.5
Aug 2010	v, t, l	118°	2.6	25.2	1020.7
Sep 2010	v	193°	4	19.2	1013.2

Table 2. Comparison of the relative contribution of monoterpenes from several possible sources near the forest floor. Resin samples have been taken in September 2010.

name	resin [%]	spruce litter [%]	pine litter [%]	soil efflux [%]
α-pinene	34.84	38.62	58.67	59.06
β-pinene	35.38	4.83	4.59	3.79
Δ^3-carene	13.91	2.07	27.04	25.91
limonene	14.8	11.03	0.51	0.24
	(this work)	(Isidorov et al., 2010)	(Isidorov et al., 2010)	(Aaltonen et al., 2011)
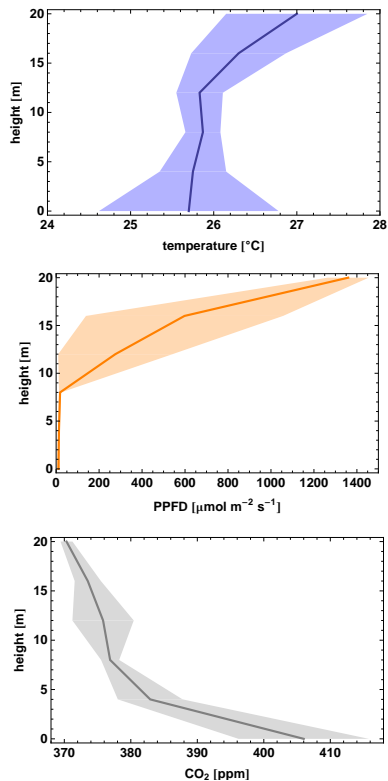
Fig. 1. Example of key environmental drivers for isoprene and monoterpene emissions from forest canopies in summer. Air temperature, quantum flux density (PPFD) and ambient CO_2 mixing ratio have been measured on the 12 August 2010. The lines denote mean values and the shaded areas the standard deviations.
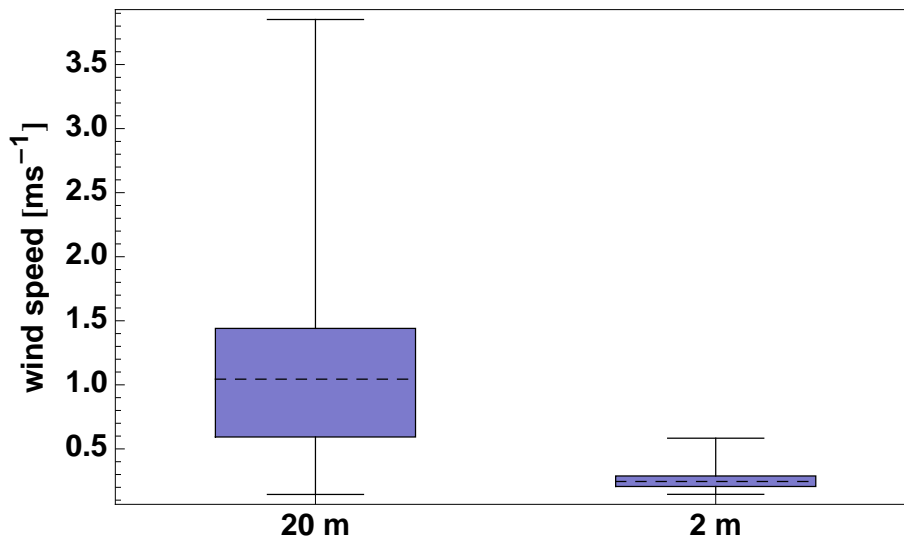
Fig. 2. Example for the variation of the wind speed above (20 m) and within the forest canopy (2 m). The data were measured during August 2009. The monthly median wind speed at 20 m height was $1.04\,\mathrm{m\,s^{-1}}$ and at 2 m height dropped to $0.25\,\mathrm{m\,s^{-1}}$. The boxes cover 50 % of the data.
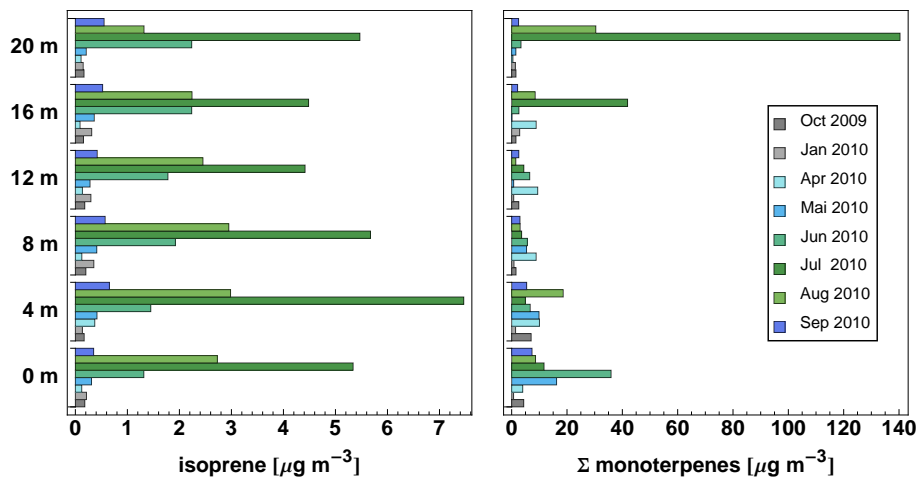
Fig. 3. Isoprene and total monoterpene concentrations measured in ambient air throughout the forest canopy and seasons. The sum of monoterpenes includes α-thujene, α- and β-pinene, camphene, Δ^3-carene and limonene (see also legend Fig. 5).
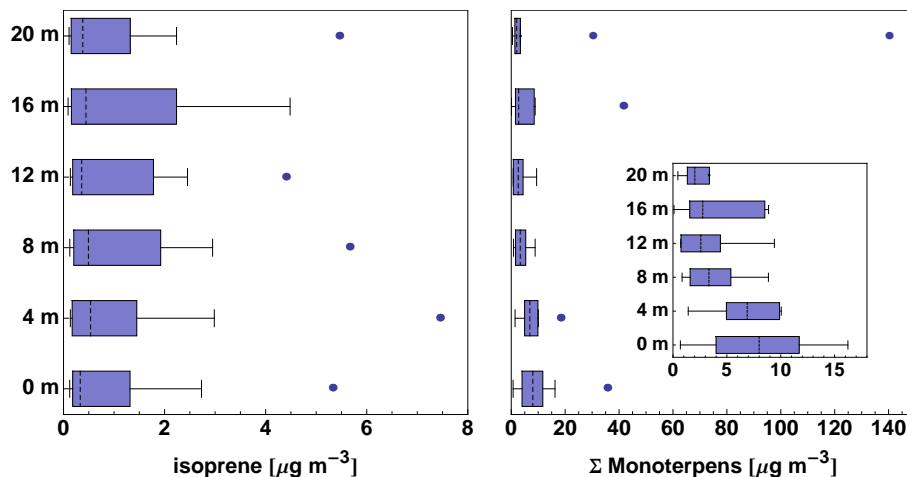
Fig. 4. Variation of isoprene and total monoterpene ambient air concentrations measured over the whole year. The boxes, ranging from the 0.25 to the 0.75 quantile, cover 50 % of the data, the dashed lines denote the median concentration and the whiskers show the standard deviation of the data excluding far outliers. Outliers are given as dots and mark in both cases the measurements in July 2010 with exceptional high temperatures. The inset in the monoterpene plot show the shape of the boxes and the location of the median concentrations in detail.
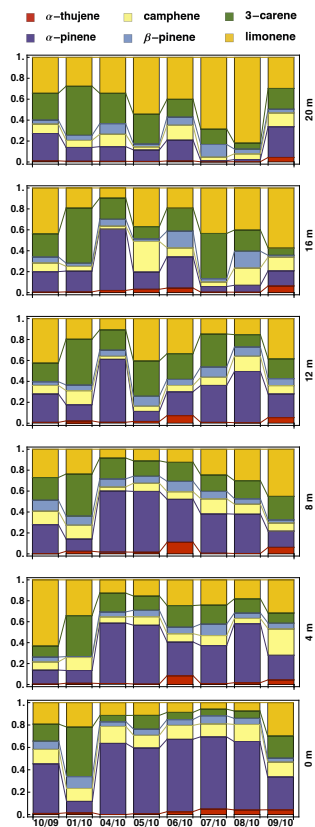
Fig. 5. Spatial and temporal relative contribution per monoterpene species scaled to the total monoterpene concentration.