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Annual variations of atmospheric VOC concentrations in a boreal forest

Hannele Hakola[1)], Heidi Hellén[1)], Virpi Tarvainen[1)], Jaana Bäck[2)],
Johanna Patokoski[3)] and Janne Rinne[3)]

1) *Finnish Meteorological Institute, Air Quality Research, P.O. Box 503, FI-00101 Helsinki, Finland*
2) *Department of Forest Ecology, P.O. Box 27, FI-00014 University of Helsinki, Finland*
3) *Department of Physics, P.O Box 64, FI-00014 University of Helsinki, Finland*

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Ambient atmospheric concentrations of monoterpene compounds were measured above a boreal forest in Hyytiälä, Finland during 2000–2007. For most of the time, two samples per week were collected, although there are some gaps in the data due to analytical or other issues. The monoterpene concentrations reached their maximum in summer, although they were found to be quite high also during winter. The main compounds found during winter were α-pinene, Δ^3-carene, β-pinene and camphene. In summer 1,8-cineol and sabinene were also present in the samples. The concentrations of α-pinene, β-pinene/myrcene, camphene, Δ^3-carene increased during the measurement period both in winter and in summer. This increase cannot be explained by meteorological conditions. The possible explanations could be human activities in the vicinity of the sampling site in addition to forest growth. The seasonal cycles of daytime concentrations were found to follow emission fluxes modeled using a simple temperature dependent parameterisation. The measured monoterpene concentrations were used, together with emission rate measurements, for estimating ambient atmospheric β-caryophyllene concentration which cannot be directly measured due to its high reactivity against ozone.

Introduction

Volatile organic compounds (VOCs) present in the atmosphere are interesting for several reasons. The VOCs participate in ozone formation and destruction reactions and they also contribute to new particle formation and growth processes (Chameides *et al.* 1992, Kulmala *et al.* 2004, Tunved *et al.* 2006, Bonn *et al.* 2008), thus affecting both local and regional air quality and climate (Goldstein and Galbally, 2007, Spracklen *et al.* 2008). Knowledge of the sources and emissions of both anthropogenic and biogenic VOCs as well as their concentrations is essential for developing efficient ozone control and climate change abatement strategies.

The ambient air concentrations of volatile organic compounds have been measured campaign-wise at rural forest sites in boreal conditions (Hakola *et al.* 2000, Ruuskanen *et al.* 2009). In general the results suffer from short measurement periods and lack of continuity in the measurement procedures. Our hypothesis was that frequent, year-round VOC concentration measurements in a forest environment can reveal changes in ecosystem VOC exchange at seasonal and inter-annual time scales and thus are particularly useful in estimations of the regional VOC emissions. Therefore we aimed at long-term measurements with frequent sampling intervals in a representative boreal coniferous forest stand.

We report the ambient concentrations of biogenic VOCs measured from April 2000 to November 2007 at the SMEAR II (Station For Measuring Forest Ecosystem–Atmosphere Relations 61°51´N, 24°17´E, 181 m a.s.l.) measurement station located in Hyytiälä, southern Finland. To our knowledge, this is the first VOC time series covering several years and enabling a detailed study of the annual variability of the monoterpene concentrations.

Methods

At the SMEAR II site, the nearest vegetation is a homogenous, seed-propagated 40-year-old Scots pine (*Pinus sylvestris*) stand with some deciduous understorey trees sparsely located in-between. In the footprint area, there are mature stands of Scots pine, Norway spruce (*Picea abies*), with some silver birch (*Betula pubescens*), aspen (*Populus tremula*) and willow (*Salix* sp.). The total leaf mass (LMA) in the footprint area is ca. 600 g m^{-2}, however closer to the measurement point the proportion of pine is large and thus there the LMA is around 400 g m^{-2}, giving a leaf area index (LAI) value around six. The air sampling was done initially above the canopy on the upper level of a scaffolding tower. During the measurement period, the average Scots pine canopy height in the footprint area increased by 2.1 m, from 15.1 m to 17.2 m, and the average annual height growth was 0.3 m.

Sampling was started in April 2000 and continued until November 2007. There are few larger gaps in the data due to analytical or other problems. These are: January–April 2001, May–June and August–December 2002, April–May 2003 and July 2006. The air samples were collected on adsorbent tubes filled with Tenax-TA and Carbopack-B using pumped sampling. During the first years constant flow type pumps with mass flow controllers were used (SKC), but since August 2004, a critical orifice attached to the pumps was used to regulate the flow more constant. The sampling flow was checked each day before conducting the sampling. The flow rates with constant flow pumps were about 100 ml min^{-1} and with critical orifices 60 and 70 ml min^{-1} for parallel samples. The sampling time was about 30 min until the end of January 2002 and about 60 min after that. The samples were collected about three times a week, two samples at a time, always around noon. Thus, especially during the summertime the measurements represent the lowest monoterpene concentrations during a diurnal cycle (Ruuskanen *et al*. 2009).

Two MnO_2-coated copper nets placed in a Teflon® holder were employed in front of the sampling tubes to destroy ozone. The MnO_2 nets were tested and they were found to remove about 80% of the ozone and yet not remove α-pinene, β-pinene, limonene or Δ^3-carene. About 10% of camphene was removed due to the nets and linalool was removed totally. So, even if linalool existed in ambient air, it would not have been detected in our measurements.

The adsorbent tubes were analysed using a thermodesorption instrument (Perkin-Elmer ATD-400) connected to a gas chromatograph (HP 5890) with HP-1 column (60 m, inner diameter 0.25 mm) and a mass-selective detector (HP 5972). Samples were concentrated in the thermodesorption instrument in a cold trap (–30 °C) filled with Tenax-TA. Samples were analysed using the selected ion mode (SIM). The analytical system did not allow the separation of myrcene and β-pinene; their amount was therefore expressed as a sum and quantified as β-pinene. Five-point calibration was utilised using liquid standards in methanol solutions. Standard solutions were injected onto adsorbent tubes that were flushed with helium or nitrogen flow (100 ml min^{-1}) for five minutes in order to remove methanol. The detection limits were 10–200 ng m^{-3} for most of the compounds.

Results and discussion

The monoterpene concentrations

Seasonal dynamics

As was found already earlier (Hakola *et al*. 2000,

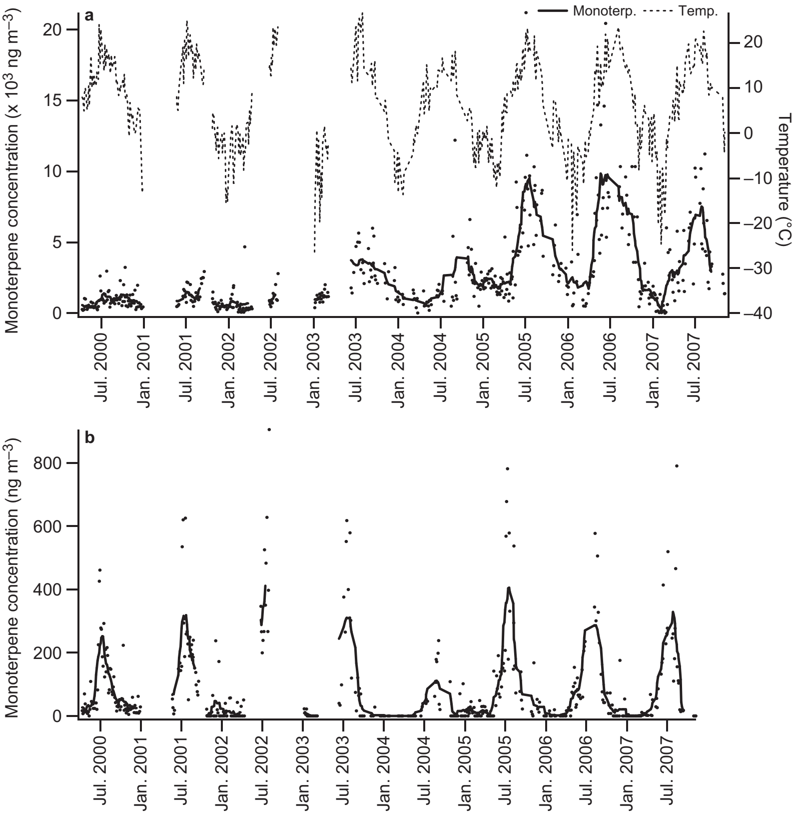

Fig. 1. The sum of concentrations of α-pinene, β-pinene/myrcene, camphene and Δ^3-carene (upper panel) and the sum of concentrations of sabinene and 1,8-cineol (lower panel), together with a 10-day moving average. Temperature is shown in the upper panel.

2003), monoterpene concentrations in the air reached their maximum in June–August (Fig. 1). This is due to stronger biogenic emissions in summer (Hakola *et al.* 2006). Concentrations of α-pinene, β-pinene, and Δ^3-carene were well correlated with each other (R^2 = 0.64 and 0.87 for the correlation of α-pinene and β-pinene, and α-pinene and Δ^3-carene, respectively). Their concentrations started increasing simultaneously in May–June, as well as did the concentration of camphene, and they declined at the end of August. However, the concentrations of sabinene and 1,8-cineol started increasing later, in the end of June, and they also declined earlier, in the beginning of August. Although ambient concentrations of sabinene and 1,8-cineol were detectable almost only in summer, they were not well correlated and they were likely to have different sources. 1,8-cineol has been found in the emissions from Scots pine growing in the same area (Hakola *et al.* 2006), whereas sabinene has been detected in the emission of birches (Hakola *et al.* 2001).

Between-year variations

The most striking feature in the observed concentrations (Fig. 1 and Table 1) was the increase of the concentrations of α-pinene, β-pinene/myrcene, camphene and Δ^3-carene towards the end of the measurement period. The concentrations were increasing both in winter and in summer. However, increase in summer was clearly higher than in winter. Average increase/year for α-pinene as compared with values in 2000 was 200% in summer and 60% in winter. These concentrations had increased steadily until 2006, but in 2007 they slightly declined from the maximum values. Winter concentrations decreased to the levels of the first years, but summer values were still clearly higher. The concentration of α-pinene increased most, 500 ng m^{-3} a^{-1}. For the β-pinene/myrcene, camphene and Δ^3-carene the average increase was 17, 14 and 163 ng m^{-3} a^{-1}, respectively. Therefore, the relative contribution of α-pinene also increased from 49% in 2000 to 69% in 2007. The relative contribution of all the other monoterpenes was decreasing, about 1%–6% each. Limonene was not presented due to unacceptable blank levels in 2002–2005.

The reason for the concentration increase of most of the monoterpenes is not clear. The sampling had been conducted on the original tower until November 2004, after which it was moved to another measurement tower of about equal height at a distance of about 20 meters from the original place, and back again in September 2006. However, the distance between the towers is not large and the forest around them is similar. One possible reason for the observed concentration increases is the height growth of the closest trees. While in the beginning of the measurement period the point where air was sampled was situated close to the uppermost branches, the gradual growth of the trees (ca. 30 cm a^{-1}) resulted in an increasing influence of the nearest branches. This might explain the increased concentrations of the major emitted compounds, α-pinene and Δ^3-carene. However, the reason for the stable level of other compounds remains unclear. The compounds whose concentrations rose are those that are presumably stored in plant compartments, especially in resin ducts and in other permanent reservoirs. Sabinene and 1,8-cineol were observed almost only during summer and they have not been reported to be stored in the Scots pine needles in substantial amounts (Kainulainen and Holopainen 2002, Isidorov *et al.* 2003, Kupcinskiene *et al.* 2008), therefore their emissions from the vegetation may be more directly related to *de novo* biosynthesis.

Because sabinene and 1,8-cineol concentrations did not rise, we may also hypothesize that the reason is not only the increase of the

Table 1. The annual mean, summer (June–August) and winter (Jan., Feb., Dec.) concentrations (ng m^{-3}) of the monoterpenes, number of measurements (*N*) and standard errors of the means (SE). The July data from 2002 is missing. The limonene data is not presented due to analytical problems in 2002–2005.

	N	α-pinene		β-pinene/ myrcene		Camphene		3-carene		Sabinene		1,8-cineol	
		Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
2000	76	460	40	110	10	60	0	250	20	30	10	50	10
2001	51	560	60	120	10	50	10	310	30	60	10	70	10
2002	40	450	90	100	10	30	10	230	30	40	10	90	20
2003	47	1500	130	160	20	120	20	570	60	30	10	50	20
2004	52	1190	180	130	20	80	10	520	80	20	0	10	0
2005	78	2900	260	190	20	140	20	1050	90	30	10	60	10
2006	69	3470	330	200	20	120	10	1230	140	30	10	40	10
2007	62	2360	260	130	10	100	10	760	90	50	10	40	10
Summer													
2000	27	480	50	140	30	60	10	310	40	70	10	90	20
2001	20	670	50	160	20	30	10	400	40	140	20	120	20
2002	12	620	100	140	30	60	20	350	50	140	30	270	30
2003	13	2150	240	240	30	210	20	840	120	100	20	170	40
2004	11	970	270	120	20	90	20	480	110	50	10	10	10
2005	21	5450	560	330	40	300	30	1800	210	110	20	160	30
2006	13	6310	670	340	30	180	20	2460	440	150	30	100	10
2007	20	4330	310	240	10	160	10	1460	100	140	0	110	10
Winter													
2000	8	330	110	80	20	70	10	200	60	0	0	20	10
2001	8	200	20	70	10	60	20	140	10	0	0	50	30
2002	16	340	90	90	10	20	10	180	40	0	0	10	10
2003	20	880	90	90	20	30	10	280	30	0	0	0	0
2004	12	950	130	80	10	30	20	420	80	0	0	10	10
2005	21	1490	90	130	10	70	20	630	40	0	0	10	0
2006	14	1440	330	110	30	70	10	450	110	0	0	0	0
2007	24	380	100	40	10	60	10	130	20	0	0	0	0

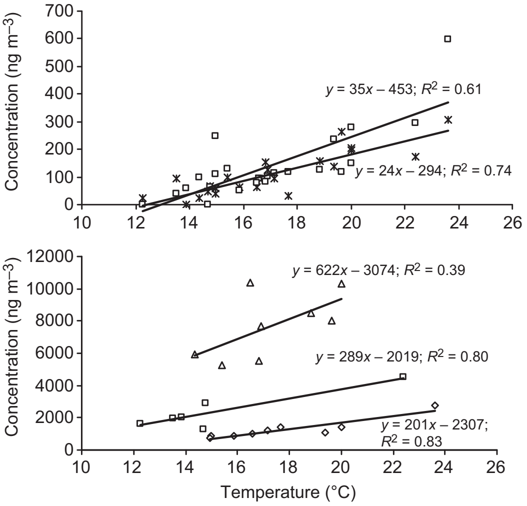

Fig. 2. Upper panel: monthly mean concentrations of sabinene (asterisks) and 1,8-cineol (squares) *vs.* monthly mean temperature. Lower panel: monthly mean concentrations of sum of α-pinene, β-pinene/myrcene, camphene and Δ^3-carene *vs.* monthly mean temperature. The data is divided into three groups: 2000–2002 (diamonds), 2003–2004 (squares) and 2005–2006 (triangles). The figures contain data from summer months only (June, July, August).

monoterpene emissions of nearby trees, but other activities in the area. In November 2004, a mixed stand of about 1 ha with mostly Scots pine and Norway spruce had been logged only about 200 m from the site. The following April the slash and tree stumps were removed and the ground was mounded. The tree stumps remained in the vicinity of the logged area until November 2006. Forestry operations have been observed to influence the concentrations in the near vicinity of the operated stand (Räisänen *et al.* 2008), and, therefore, these operations could have had an influence on the steeper rise in concentrations that took place in spring 2005. In 2005, a new log cottage was also built at the sampling site and the construction work may also have affected the local monoterpene concentrations. However, the first concentration increase took place earlier than either of the above mentioned operations, already in 2003. Also, the monoterpene concentrations did not show any marked wind-direction dependence which could support the influence of these above mentioned activities. During the July 2003 sampling days, the weather was warm and sunny. The mean temperature on July measurement days was 24 °C and the mean photosynthetically active radiation was 1119 μmol m^{-2} s^{-1} and the increase in 2003 could be due to higher emission rates at that time.

The effect of meteorological factors on monoterpene concentrations

The effects of meteorological factors such as temperature, radiation, relative humidity and wind speed on the monoterpene concentrations were studied, but no significant correlations were found when individual measurements were taken into account. This is due to several processes working simultaneously. The emissions are strongest, when temperatures are high, but then also the sink reactions are fastest and the boundary layer, into which the emitted compounds are diluted, is at its deepest. However, when monthly mean measurements are considered, some dependencies can be found. The monthly mean daytime concentrations of sabinene and 1,8-cineol are correlated with the monthly mean temperature in summer with $R^2 = 0.74$ and 0.61, respectively (Fig. 2). Also, the rest of the monoterpenes α-pinene, β-pinene, camphene and Δ^3-carene correlated with temperature in summer, but only when the concentration data were divided into three different groups according to period: 2000–2002, 2003–2004 and 2005–2007. The correlation coefficients (R^2) for the sum of the four monoterpenes and temperature were 0.83, 0.80 and 0.39 in the three periods, respectively (Fig. 2). So, the monoterpene concentration increase from 2000 to 2006 is not due to increased temperature, but likely due to stronger emission sources nearby.

The effect of rainfall on the monoterpene concentrations was studied as well. Summers 2004 and 2005 were rainy. The amount of rainfall for summer months (June, July and August) was 307 and 309 mm for the years 2004 and 2005, respectively. In summer 2006 the rainfall was smallest, 137 mm. The concentrations of the sum of all monoterpenes were very different between the two rainy summers 2004 and 2005: 1714 and 8156 ng m^{-3}, respectively. In the dry summer 2006, the mean concentration sum was the highest, 9545 ng m^{-3}. On the basis of this data, the amount of rainfall does not seem to affect the monoterpene concentrations, at least not directly. However, this study is potentially biased by the fact that the samples were never taken during heavy rain.

Estimating the sesquiterpene concentration

Most of the sesquiterpenes, especially β-caryophyllene which is the main sesquiterpene emitted by Scots pine, are so reactive towards ozone that they cannot be measured in the ambient air. Their reaction products are believed to participate in the formation and growth processes of atmospheric aerosols (Bonn and Moortgat 2003, Lee *et al.* 2006) and in order to calculate the nucleation and growth rates of particles caused by these compounds, the ambient concentration of the precursor sesquiterpenes should be known. Bonn *et al.* (2007) calculated the sesquiterpene concentrations using the atmospheric air ions between 0.56 and 0.75 nm in diameter. They propose these ions consist predominantly of stabilized Criegee Intermediates (sCIs) formed by the reaction of sesquiterpenes with ozone.

Based on our concentration data combined with the emission rate data from 2004 (Hakola *et al.* 2006), we evaluated the concentration of β-caryophyllene in the ambient air. We assumed a stationary state in which the emissions of α-pinene and β-caryophyllene are in equilibrium with the respective oxidative removal rates. Here we further assume that both compounds are uniformly mixed within the boundary layer and that their mixing is equal. Therefore, we can write the emission ratio to equal the oxidative removal,

$$\frac{E_{\mathrm{ST}}}{E_{\mathrm{MT}}}=\frac{k_{\mathrm{OH}}^{\mathrm{ST}}[\mathrm{OH}][\mathrm{ST}]+k_{\mathrm{O3}}^{\mathrm{ST}}[\mathrm{O_3}][\mathrm{ST}]}{k_{\mathrm{OH}}^{\mathrm{MT}}[\mathrm{OH}][\mathrm{MT}]+k_{\mathrm{O3}}^{\mathrm{MT}}[\mathrm{O_3}][\mathrm{MT}]} \quad (1)$$

Here E_{MT} and E_{ST} are the emission rates of mono- and sesquiterpenes. $k_{\mathrm{OH}}{}^{\mathrm{MT}}$ and $k_{\mathrm{OH}}{}^{\mathrm{ST}}$ are the reaction rate constants of mono- and sesquiterpenes (in this case α-pinene and β-caryophyllene) in relation to the OH radical reaction and $k_{\mathrm{O3}}{}^{\mathrm{MT}}$ and $k_{\mathrm{O3}}{}^{\mathrm{ST}}$ are the respective ozone reaction rate constants. The equation can be solved to yield the β-caryophyllene concentration [ST] as the other variables are either measured or can be taken from literature. The OH radical and ozone concentrations used in the calculation are taken from Hakola *et al.* (2003), and they are given in Table 2 together with the estimated β-caryophyllene concentrations. Since the forest where the samples were taken is mainly pine forest, we used the emission rates for Scots pine (Hakola *et al.* 2006) in the calculation. The β-caryophyllene concentrations were estimated using α-pinene concentrations and emission rates (Table 2). As expected from the high reactivity of β-caryophyllene, the concentration in the ambient air would be quite low, about 20 ng m^{-3} in the high emission season, which is too small to be measured using current techniques. Bonn *et al.* (2007) estimated higher sesquiter-

Table 2. Monthly-mean emission rates of Scots pine used for estimating β-caryophyllene concentrations and measured α-pinene concentrations. The OH radical and ozone concentrations used in the calculations are from Hakola *et al.* (2003).

	Emission rate		α-pinene (ng m^{-3})	β-caryophyllene (ng m^{-3})	OH (ppt)	O$_3$ (ppb)
	α-pinene (ng g(dw)$^{-1}$ h^{-1})	β-caryophyllene (ng g(dw)$^{-1}$ h^{-1})				
April	33	1	561	0.15	0.030	42
May	91	11	305	0.50	0.058	44
June	90	29	985	4.66	0.063	39
July	67	161	687	23.9	0.058	36
August	52	42	1209	12.9	0.035	28
Sept	18	3	2435	4.39	0.029	30

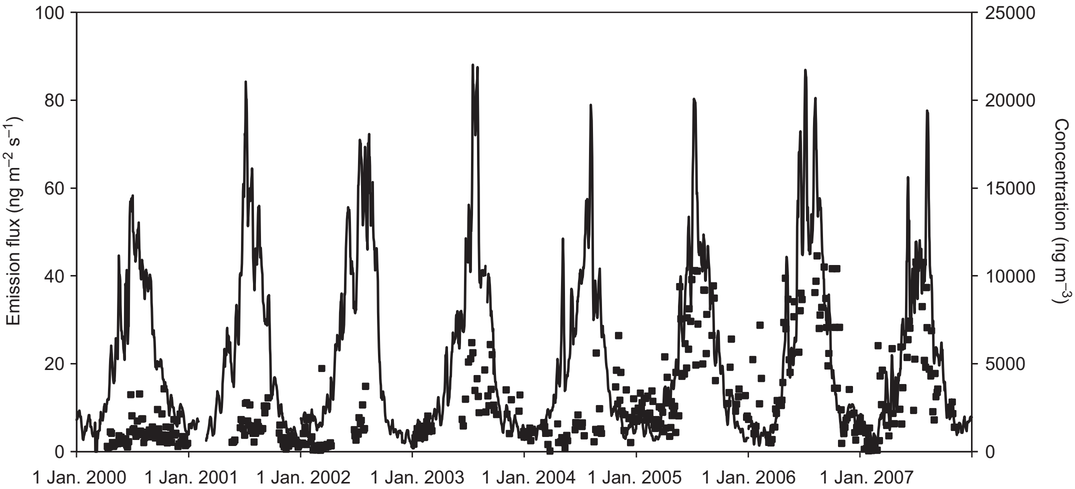

Fig. 3. Seven-day moving average monoterpene emission flux (solid line) and the observed total monoterpene concentrations (black squares) during the measurement period in Hyytiälä.

pene concentrations during summer (up to about 1 μg m^{-3}), but this would include also other sesquiterpenes. Their estimates for spring concentrations were also low, below 10 ng m^{-3}.

Emission model calculations

The most likely source of monoterpenes measured in forest air, are emissions from the forest itself. Therefore, the terpenoid (monoterpene, isoprene and sesquiterpene) emissions from the forest in a 10 × 10 km square around the SMEAR II measurement site were calculated with a simple BEIS-type emission model driven by hourly meteorological data, following the methodology described in detail in Lindfors and Laurila (2000), Lindfors *et al*. (2000) and Tarvainen *et al*. (2007). The modeled daily average monoterpene emission fluxes during 2000–2007, together with observed total monoterpene concentrations, are shown in Fig. 3. Especially during the latter half of the measurement period there are clear similarities between the seasonal variation of the emission fluxes and the concentrations, with the intense emission peaks predicted by the emission model reflected in the concentration maxima. During the early years, however, the consistency is less striking, indicating that there are also many other factors than just emissions affecting the observed concentrations. As the emission model takes into account only temperature and solar radiation as its driving parameters, environmental factors such as wind conditions, precipitation, and drought, physical disturbance of the plants by e.g. herbivore attacks, or chemical influences such as oxidant concentrations, which may affect the emissions and the mixing and transport of the emitted compounds, are not included. The improved consistency between emission fluxes and observed concentrations in the later years does suggest, however, that the effect of local forest emissions on the measured concentrations became stronger during the measurement period as the forest had grown and therefore the measurements more truly represent the air inside the forest canopy and not so much the air above it.

The modeled monthly average sesquiterpene emission fluxes are shown in Fig. 4 together with the estimated β-caryophyllene concentrations, and even though both the sesquiterpene emission model and the concentration estimate are still only suggestive, there appears to be consistency in the seasonal behavior of sesquiterpenes. As these compounds are very reactive and thus cannot be transported far from their place of origin, the variation of the minute amounts of sesquiterpenes present in the forest air should be even more closely linked to their local emission patterns than the monoterpene concentrations. Based on these indicative results, it appears that

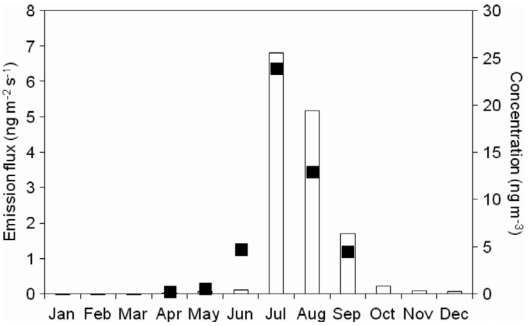

Fig. 4. Modeled monthly average sesquiterpene emission fluxes (bars) and the estimated β-caryophyllene concentrations (black squares) at the SMEAR II site.

both sesquiterpene emissions and concentrations are very low in spring and early summer, reach a maximum in July–August and decline again in the autumn.

Conclusions

We present a uniquely long time-series of daytime ambient atmospheric concentration measurements of terpenoid compounds in a boreal coniferous ecosystem. The dataset clearly shows that long-term measurements are necessary to reveal significant variations in annual patterns of concentrations, which are influenced by both biogenic and meteorological factors.

The main observed compounds were α-pinene, β-pinene/myrcene, camphene and Δ^3-carene. Additionally, sabinene and 1,8-cineol were observed in summer. The concentrations of most of the monoterpenes increased during the measurement period both in winter and in summer. This increase was not explained by meteorological conditions. The possible explanations in addition to forest growth could be human activities in the vicinity of the sampling site. Therefore, standardizing the sampling position in relation to vegetation and diurnal timing of measurements should be carefully considered.

The measured monoterpene concentrations can also be used for calculating concentrations of compounds which are difficult to measure, such as sesquiterpenes, if their proportional emission strengths are known.

There are clear similarities between the seasonal variation of the modeled emission fluxes and the observed concentrations, especially during the latter half of the measurement period due to stronger effect of local emissions as the forest has grown and the measurements more truly represent the air inside the forest canopy and not so much the air above it.

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