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New foliage growth is a significant, unaccounted source for volatiles in boreal evergreen forests

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Abstract

Estimates of volatile organic compound (VOC) emissions from forests are based on the assumption that foliage has a steady emission potential over its lifetime, and that emissions are mainly modified by short term variations in light and temperature. However, in many field studies this has been challenged, and high emissions and atmospheric concentrations have been measured during periods of low biological activity such as in springtime. We conducted measurements during three years, using an online gas-exchange monitoring system to observe volatile organic emissions from a mature (1 yr old) and a growing Scots pine shoot. The emission rates of organic vapours (monoterpenes, methyl butenol (MBO), acetone and methanol) from vegetative buds of Scots pine during the dehardening and rapid shoot growth stages were one to two orders of magnitude higher than those from mature foliage. The normally assumed temperature dependency was not sufficient to explain the variations in emission rates during spring. The diurnal emission pattern of growing shoots differed from the diurnal cycle in temperature as well as from the diurnal emission pattern of mature shoots, which may be related to processes involved in shoot or needle elongation. Our findings imply that global estimations of monoterpene emission rates from forests are in need of revision, and that the physiological state of the plants should be taken into account when emissions of the reactive gases such as monoterpenes are estimated. The significant interannual variation in emission rates, related to changes in plant metabolic activity, has important implications to the aerosol precursor concentrations and chemical reactions in atmosphere, and potentially offers an explanation for the frequent aerosol formation events in spring.

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1 Introduction

The current understanding on the role of biogenic feedbacks to atmospheric reactivity involves large uncertainties. The measured atmospheric concentrations of many reactive gases, for example terpenoids (mainly isoprene, mono- and sesquiterpenes), exhibit huge spatial and temporal variations due to factors related to large variation in emission rates and emission composition between or inter-species (Kesselmeier and Staudt, 1999; Bäck et al., 2012), to light and temperature-related variations in incident emission rates (Gunther et al., 1993; Komenda and Koppman 2002; Tarvainen et al., 2005) as well as to transport and chemical reactions in the air (Rinne et al., 2007). Longer term variations, due to for example leafing and senescence of foliage, have also been recognized to affect the emission rates (Karl et al., 2003; Hakola et al., 2006; Geron and Arnts 2010), the maximum rates being observed in the midsummer when leaves are fully mature.

The current models for global terpenoid emission rates are mainly using emission potentials defined for mature foliage under standard (constant) conditions, and up-scaled with biomass estimates for specific plant functional types and their regional distribution as well as modified with the prevailing irradiation and temperature ("Guenther approach", Guenther et al., 2006, 2012). However, these semi-empirical algorithms are not accounting for many inherent plant physiological processes that may produce large seasonal variations in the synthesis and emission rates of terpenoids, and thus the different model estimates have large uncertainties in total emission rates (Arneth et al., 2008; Niinemets et al., 2010). The few models empirically replicating the seasonal phenomena still assume no dependence of emission potential on leaf developmental stage in evergreen plants (Staudt et al., 2000), or use an arbitrarily defined scaling factor for modifying the emission rate according to leaf age (Guenther et al., 2012). Further, these models are concentrating mainly on isoprene, whereas model development describing the emissions of monoterpenes or oxygen-containing compounds (methanol, acetone) has been less successful (Arneth et al., 2008; Galbally and Kirstine, 2002),

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although especially in evergreen vegetation these compounds may form up to 90 % of emissions.

In all ecosystems, the annual cycle of perennial vegetation includes both active and inactive periods, which involve profound modifications in processes at molecular, cellular and organ scale. In boreal evergreens the increased freezing tolerance – a prerequisite for sustained foliage retention – is provided by hardening in the fall. Hardening leads to an inactive rest period (dormancy) in both mature foliage and in newly formed buds housing the next year's annual growth. The driving factor for dormancy release and subsequent metabolic activation in both mature tissues and developing buds is temperature change (Rohde and Balerao, 2007; Hänninen et al., 2007). The recovery from dormancy, re-activation of metabolism and onset of growth in spring take place in two phases: the release of true dormancy leads first to a quiescent phase lacking any visible signs of growth, and only when dormancy is fully released the new growth can start. In the quiescent phase, environmental cues activate the expression of genes encoding enzymatic pathways to synthesize new macromolecules for growth (Heide, 1993; Rohde and Balerao, 2007; Sutinen et al., 2009). During the active period, biomass growth takes place by formation of new tissues in meristems, involving the formation, differentiation and expansion of new cells, tissues and organs. Such phenological events require environmental cues which activate the enzymatic pathways leading to synthesis of new macromolecules for growth (for example lignin and pectin for cell walls, carotenoids and chlorophylls for thylakoids, and lipids and proteins for cell membranes). Despite their great significance for vegetation, these strong turning points of the key metabolic processes have not been implemented in emission estimates so far.

We were motivated by the knowledge that atmospheric aerosol formation and growth are closely linked to concentrations of their organic precursors (e.g. terpenoids), originating from biosphere processes (Kulmala et al., 2013). It is well documented that in a wide variety of environments, the aerosol formation events are peaking in springtime (Dal Maso et al., 2005; Manninen et al., 2010), but the reasons for this are still unclear. We hypothesized that we would observe high VOC emission rates from Scots pine

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branches in spring, and that the high spring emissions would be related to dormancy release and growth initiation in vegetative buds. To study this, we set up to measure the seasonal and diurnal patterns in emissions in both mature and growing foliage of Scots pine trees in field conditions, using an automated enclosure system with sufficient time resolution.

2 Material and methods

2.1 Smear II measurement station

The measurements were conducted at the SMEAR II measurement station (Station for Measuring Forest Ecosystem – Atmosphere Relations) in Hyytiälä, southern Finland (61° N, 24° E, 180 m a.s.l.). The forest at the station is dominated by Scots pine (*Pinus sylvestris* L.), and represents a managed boreal coniferous forest site with closed canopy. The stand was established after prescribed burning conducted in 1962. Currently the canopy reaches a height of ca. 17 m, with living canopy height ca. 7 m and one sided leaf area index (LAI) 2–2.5 $m^2\,m^{-2}$. With a scaffolding tower we have access to the top of the canopy where the enclosure measurements are located in the top whorls. More details about the site are given in Hari and Kulmala (2005).

2.2 Emission measurements

The shoot gas exchange was measured with an automated gas-exchange system, consisting of two cylindrical shoot enclosures (Fig. 1), sampling tubing, and analyzers for CO_2, H_2O and VOCs (Altimir et al., 2002). The enclosures are made of acrylic plastic and their inner surfaces are coated with fluorinated ethylene propylene (FEP) film. The enclosures remained open most of the time and closed intermittently for measurements, typically four successive 3 min periods in three hour intervals. While open, the interior was in contact with ambient unfiltered air. During a closure, air sample ($1\,dm^3\,min^{-1}$) was drawn from the enclosure to the gas analyzers along the sample

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lines. Ambient air was allowed to enter the enclosure through small holes in the chamber walls to compensate the sample air flow taken from the chamber. The air temperature inside the enclosure and photosynthetically active photon flux density (PPFD) were measured before and during the closure and the values recorded at 5 s interval, using thermocouples (copper-constantan) or PT100 as temperature and LI-COR LI-190 quantum sensor (LI-COR Environmental, USA) as PPFD recorder.

Measurements were conducted during years 2009, 2010 and 2011. Shoot enclosures (volumes 3.5 and 4.5 dm^3 Fig. 1a and b) were installed to unshaded top-canopy branches during previous mid-winter or earlier: one with a mature shoot inside (hereafter "mature shoot") and the other with only a terminal bud inside chamber (hereafter "developing shoot"). All buds of the mature shoot and all auxiliary buds of the developing shoot were gently removed about one month before the installation to avoid contamination with fresh resin flowing from the scars.

The subsample for VOC analysis (0.1 $dm^3\,min^{-1}$) was taken from a sample line with 1 $dm^3\,min^{-1}$ sample flow. During 2010 and 2011, heated fluorinated ethylene propylene (FEP) tubing (length 64 m, internal diameter 4 mm) was leading the sample air towards the CO_2 and H_2O analyzers, and the VOC subsample was taken from that line before the other analyzers. During 2009 the sample for VOC analysis was taken with a separate 50 m long FEP (i.d. 4 mm) tube with no other analyzers connected to the tube. The subsample for VOC analysis with a high sensitivity PTR-QMS (proton transfer reaction – quadrupole mass spectrometer, Ionicon Analytik GmbH, Innsbruck, Austria) was drawn through a polytetrafluoroethylene (PTFE) tube with internal diameter of 1.57 mm and length of about 5 m. For details of the maintenance, calibration and volume mixing ratio calculations of PTR-QMS, see Taipale et al. (2008). The PTR-QMS measures the total concentration of all compounds having equal mass with a resolution of 1 a.m.u. (atomic mass unit) and was operated here with 12.5 s measurement interval and integration time of 1 s amu^{-1}. The measured protonated masses and the potential contributing compounds were: M33 (methanol), M59 (acetone), M69 (dehydrated methylbutenol (MBO) fragment, hereafter MBO) and M137 (monoterpenes) (de

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Gouw and Warneke, 2007). The lower limit of detection was ca. 50–100 pptv (Taipale et al., 2008).

Calibration of the PTR-QMS was conducted 2–4 times per month using a bottled standard gas containing ca. 1 ppmv methanol, acetone, isoprene and α-pinene (Apel-Riemer Environmental Inc., USA, and Ionimed GmbH, Austria). In the calibration the standard gas was diluted close to the atmospheric concentrations (5–20 ppbv) using a catalytic converter (Parker ChromGas Zero Air Generator, model 3501, USA). The VOC emission rates were measured and calculated applying mass balance equation to the concentration change during the chamber closure (Kolari et al., 2012). The emission rate calculation was conducted per dry needle mass, which was determined at the end of each measurement period, typically in November.

The used mass spectrometer technique only distinguished compounds based on their molecular mass, and thus one mass can include several compounds or their fragments. The protonated atomic mass 69 includes both a dehydrated fragment of MBO and isoprene (de Gouw and Warneke, 2007). Many pine species (including Scots pine) are known to emit considerable amounts of MBO, but only negligible amounts of isoprene (Zeidler and Lichtenthaler, 2001; Tarvainen et al., 2005; Gray et al., 2006). Based on this, we assume that in this case the emission at 69 a.m.u. is mostly composed of the MBO fragment.

2.3 Shoot and needle elongation

In order to evaluate the influence of shoot and needle growth on emission patterns, the growth of pine shoot and needles were measured 1–3 times per week starting from the beginning of the elongation period, i.e. from the latter part of April, until September. Measurements were conducted with the help of digital photographs taken at a distance of at least two meters; the length of the shoot and 6–10 randomly chosen needles were measured from the photographs using the width of the enclosure as a scale. The theoretical accuracy of the measurement method is 0.065 mm, and practical repeatability is below 1 mm. The length of the next terminal bud (formed during July–August)

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was excluded from the shoot length results. In order to analyze the effect of enclosure environment on growth, the shoot and needle elongation was measured both inside and outside of the enclosure from 4 branches. The measured results were interpolated using a shoot and needle elongation model based on inherent growth rhythms driven by temperature (Schiestl-Aalto et al., 2013).

To obtain information about diurnal timing of shoot elongation, the shoot elongation was measured also using continuous measurement method. The shoot length change was measured using a Solartron Mach1 free carrier magnetic core with BIM interface unit (Solartron Metrology, Bognor Regis, UK). The diurnal shoot elongation pattern was measured only outside of enclosure and we suppose that the diurnal timing of shoot elongation inside enclosure closely resembles that of outside enclosure because the patterns of driving factors, mostly temperature are almost identical.

2.4 Estimation of the contribution of developing needle age class to the total canopy emission

To estimate the contribution of the developing foliage compared to the total foliage emissions, three simplifying assumptions were applied:

(i) All remaining needle age classes have the same mass per land area in the autumn. As the canopy closure has taken place several decades ago, the stand needle mass is rather constant; all needle age classes have same mass.

(ii) The oldest needle age class falls out at the same time with the elongation of the developing needle age class so that the stand needle mass is considered stable over growing season. According to Rautiainen et al. (2012) the Scots pine stand needle mass in southern Finland is relatively constant over growing season and the trees have on average three needle age classes.

(iii) All needle age classes at the same canopy height face about identical (light and temperature) environmental conditions. The canopy structure and growth mode

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of Scots pine produce almost even spatial distribution of all living needle age classes. The spatial distribution is to some extent skew so that the newest needle age class is shading the older ones, but because Scots pine canopy is fairly sparse the light and thermal conditions of all needle age classes are assumed to be almost identical.

Based on the above assumptions, the contribution of the developing needle age class to the total emissions (C_D, %) is:

$$C_D = \frac{m_D E_D}{m_M E_M + m_D E_D} \quad (1)$$

where m_D is the mass of developing needles per unit area ($g\,m^{-2}$), E_D is the VOC emission rate of the developing needles ($ng\,g^{-1}\,s^{-1}$), m_M is the mass of mature needles and E_M is the emission rate of the mature needles, units corresponding to those of developing needles. C_D is unitless. The needle mass is assumed to be directly proportional to needle length.

Conventionally the emission inventories have been based on the assumption that the developing and mature needle age classes have identical emission rates per needle mass or area (Guenther et al., 1993; Tarvainen et al., 2005). We next estimated the concealed proportion of emissions of this approach, if the high emissions from developing needles are not taken into account. The estimation is based on the reference values ER_C and ER_R representing conventional approach and our results, respectively. The reference value ER_R is:

$$ER_R = m_M E_M + m_D E_D \quad (2)$$

The reference value for the conventional approach (ER_C) was calculated as follows:

$$ER_C = m_T E_M \quad (3)$$

Where m_T is the total mass of needles per area, unit corresponding to m_M and m_D.

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The reference values ER_R and ER_C were calculated only to allow for comparison between them, not to give estimates of true stand scale emissions. We integrated the emissions of the stand both with our new method and with the conventional approach to estimate the proportion of concealed emissions in conventional approach; the estimate was obtained by dividing the cumulative reference value ER_R with the cumulative reference value ER_C.

2.5 Diurnal emission patterns

To test if the diurnal cycles in VOC emissions for mature and developing Scots pine shoots are equal, we calculated average diurnal cycles in VOC emissions from mature and developing Scots pine shoots. Data from all three years was included and three periods differing in the growth stage of needles and shoots were chosen for comparisons: (i) April (before the growth onset), (ii) most intensive needle elongation days (needle elongation rate $\geq 0{,}5\,\mathrm{mm\,d^{-1}}$), and (iii) September (after the end of growth). The emission rates during each 3 h measurement cycle (8 per day) were averaged, and only days with all 3 h cycles with data coverage 50 % or higher were accepted.

The diurnal emission data was normalized using the daily means to enable comparing the emission rates from days having unequal environmental conditions. We tested if the diurnal pattern of emissions between developing and mature shoots during each specified period of growth stage was significantly different using t test ($p \leq 0.05$), separately for each compound. The chamber temperatures were tested in the same way, to analyze the possible differences in diurnal temperature dynamics in the chambers. Depending on the compound, the number of days with sufficient data was 20–47, 35–67 and 15–39 in April, during the maximum growth period and in September, respectively.

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3 Results and discussion

3.1 The developing buds and needles as sources for volatiles

Growing leaves have previously been observed to release significantly more methanol than mature tissues (e.g. McDonald and Fall, 1993; Galbally and Kirstine, 2002; Hüve et al., 2007) due to cell wall demethylation during cell growth, and this was confirmed in our study as well. Remarkably, our measurements show that in addition to methanol, the initial phases of new biomass development in buds influence dramatically also the MBO and monoterpene emissions. The Scots pine buds became strong sources of monoterpenes, MBO, methanol and acetone already well before any measurable growth (Fig. 2a and b). This pattern was consistent over the three years' measurement period. The monoterpene emissions per unit biomass were two orders of magnitude higher from the developing shoot than from the mature, 1–2 yr old foliage in the spring, and remained at a higher level until the growth ended in late summer. The bud and developing shoot were also strong sources of MBO, methanol and acetone (Fig. 2a–d).

The monoterpene emissions from conifer tissues can originate either from preformed storage or from de novo synthesis. In mature Scots pine needles, Ghirardo et al. (2010) estimated that ca. 40 % of the emissions originated from the storage pool, but in buds or developing needles such estimates have not been reported. Furthermore, only very few data exist on even the monoterpene contents in buds. In one study in North America, the monoterpene concentration in apical buds of two pine species was 10–18 mg g(DW)$^{-1}$ (Hall et al., 2013), comparable to the mature needles of same species. Although the Scots pine buds most likely also contain significant constitutive monoterpene storage, it is unlikely that the observed extremely high emission rates would be originating solely from preformed storages. If the emissions would have been released only from storage, then the buds and mature needles should have shown similar magnitude of emission rates in identical conditions in spring. This was however not the case. Furthermore, there are no permanent storage pools for MBO or methanol in plant tissues. We therefore suggest that the reason for the extremely high monoterpene, MBO

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and methanol emission rates is the high metabolic activity in the quiescent and growing tissues (buds and developing shoots), resulting in de novo synthesis.

The availabilities of energy and carbon skeletons are the most important factors in production of VOCs in cells. Additionally, emissions of many volatile compounds are strongly correlated with corresponding enzyme activities, indicating transcriptional, post-transcriptional and enzymatic controls (Fischbach et al., 2002; Laothawornkitkul et al., 2009; Dudareva et al., 2013). The measured VOCs (terpenoids, methanol and acetone) originate from several different biosynthetic pathways, and it is ambiguous if the physiological controls of all these pathways are co-ordinated. However, it seems that they are all activated during the new biomass growth period. Owen and Peñuelas (2005) suggested that the volatile terpenoid emissions might be controlled by the same factors that control the terpenoid pathway, producing the higher molecular weight, "essential" terpenoids (Lichtenthaler, 1999). These include e.g. carotenoid pigments and gibberellins, the plant hormones regulating many developmental processes, in particular cell division and shoot elongation. Thus, it is not surprising to see also high production of volatile terpenoids at the time when the growth hormone production is highest.

The cellular processes involved in the sustained rather high emission of acetone are still ambiguous, although it is one of the most abundant compounds in e.g. Scots pine and Norway spruce emissions (Janson and de Serves, 2001). Acetone is not stored in plant tissues and its production has been linked to wounding, deterring herbivores, rapid light-dark transitions or anoxic conditions in roots (Fall, 2003; Seco et al., 2007).

Our results show that although the new shoots make up only a small biomass in the beginning of the growth period (Fig. 3a), their contribution to the total foliage emissions is large (Fig. 3c–f). To estimate the contributions of growing vs. mature shoots to whole canopy emission rates, we approximated their relative contríbutions using a model for needle and shoot. This is most clearly seen in monoterpene emissions, where the buds are the dominating source (30–75 %) in the canopy before the bud break. The contribution of buds is lower for other compounds, but nevertheless they are important

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sources of MBO, methanol and acetone in spring as well. During the most intensive needle elongation period in June and July (Fig. 3b) the elongating needles are a strong source of methanol, acetone, MBO and monoterpenes, and contribute about half or one third of the total emissions from Scots pine foliage (Fig. 3c–f). Only when both the shoots and needles are fully grown in early August, the contribution of current year needles to the total emissions from the foliage is approximately equal with mature shoots.

The large monoterpene emissions from buds imply that the growing foliage is a significant source for aerosol precursors in spring, which has never been shown earlier. Based on our results, if the emissions in spring and early summer are estimated based on old foliage alone, the annual cumulative monoterpene emissions from the pine stand are only 50 % of that when the growing foliar biomass is taken into account. Further, when shorter periods are investigated the difference between the two estimates becomes significantly higher, especially so during the most intensive new shoot and needle biomass growth. By the end of thermal growing season (in the middle of October) the cumulative "concealed" proportion of emissions – that is, the emissions that aren't taken into account, compared to the assumption that all needles are emitting like mature needles – is on average 11 % for methanol, 21 % for acetone, 28 % for MBO and 98 % for monoterpenes. Further, if only the first half of growing season is taken into account – the period from the end of April to the end of June – the corresponding cumulative missing emissions are 29 %, 45 %, 50 % and 200 %, respectively.

In boreal evergreen conifers with a single flush per year, such as in Scots pine, the new foliage growth lasts about 100 days, and is characterized by a rather short and intensive shoot and needle elongation period (Fig. 4). However, in many other ecosystems, both evergreen and deciduous tree species can have several flushes (e.g. loblolly pine, longleaf pine and red oak), or are freely flushing (e.g. many birches, elms), and thus these species and ecosystems may have several high-emission periods in a growing season. What is more important, many of these species – e.g. many oaks and pines – have extremely high isoprene or monoterpene emission potentials (Hewitt

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et al., 1999). If the control of emissions in growing biomass is closely related to cell growth processes, then the ecosystem-scale emissions in e.g. mid-latitudes or in tropical region, with more or less constantly growing foliage, may reflect the growth induced isoprene emissions rather than the normal light and temperature dependent emissions.

While the characterization of vegetation types in the widely used global emission models (Guenther et al., 1995, 2012; Naik et al., 2004; Lathiere et al., 2006) does not include any speciation between the shoot growth patterns, these models are missing such large endogenous variations in emission rates. Thus the model approaches using light and temperature as drivers for emissions may or may not agree well with measurements, but the underlying biological processes are not captured with the use of only these environmental drivers. Most global monoterpene and isoprene emission estimates are derived either by scaling up the leaf-level responses to ecosystem types, or by simulating vegetation with a dynamic vegetation model, and attribute the variations in emissions only to changes in the amount of emitting leaf biomass, neglecting to account for variations in emission strength with leaf age (Guenther et al., 2006; Monson et al., 2012; Oderbolz et al., 2013). Furthermore, in the most advanced leaf-algorithm the change in emission rate with leaf age is only been taken into account as fractional adjustments embedded in the "Leaf age emission activity factor" (Guenther et al., 2012), without a defined physiological basis for the change in the activity factor over seasons.

Measuring reactive gases in field conditions is challenging. The accuracy of a dynamic enclosure system was determined by Kolari et al. (2012) to be in the range of 5–30 %, and thus the values obtained with such system may be slightly lower than the actual emission rates. The accuracy should, however, not be different between bud and mature shoot enclosures having similar measurement setups. The enclosure systems evidently cause higher temperatures affecting growth inside the enclosures, and thus direct comparisons with shoots growing in free air may be biased. In order to analyze the effect of enclosure environment on growth, we measured the shoot and needle elongation both inside and outside of the enclosure. Inside the enclosure the onset of

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shoot elongation took place during the last two weeks of April in all years (Fig. 4a and b) and the shoot elongation ended in the middle of June. The onset of needle elongation inside the enclosure (Fig. 4c and d) took place from a couple of days to two weeks later than that of shoot elongation, and continued until mid-August. Outside the enclosure (Fig. 4e–h) the growth onset occurred practically at the same time, but both the shoot and needles reached their full length 2–14 days later than inside. Also, although the shoot and needle growth rates closely resembled each other, their actual growth rates were different. The elongation rates inside the enclosure were about twofold compared with the elongation rates outside the chamber, most likely due to the more favorable conditions inside the enclosure. However, since the above reported emission rates are calculated based on actual leaf mass or area of the enclosed shoot, the incident growth rates do not affect our main results. The enclosure temperature naturally may affect the VOC emission rates from tissues due to the effect on volatilization. This effect should be similar of magnitude for both mature and growing shoots and thus its influence on the relative emission rates is insignificant.

3.2 Diurnal emission patterns

Diurnal variations of BVOC emissions have mostly been connected to short-term variations in prevailing environmental conditions, most importantly to the diel changes in light and temperature. Our results from mature shoots support these previous results: emissions follow temperature and/or photosynthetically active radiation, and reach their maximum typically during early hours of afternoon and minimum in nighttime (Fig. 5). Stomata control for emissions of the water soluble methanol from foliage, so that emissions typically show a pronounced burst when stomata open in the morning (e.g. Niinemets and Reichstein, 2003; Huve et al., 2007). The less water-soluble isoprenoids are not as much controlled by stomatal actions, and their emission rates follow light only (MBO) or light and temperature (monoterpenes), influencing production and volatilization, respectively. Like seasonal emission patterns, also the diurnal patterns have pre-

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viously only been studied in fully expanded leaves, and thus it is unknown how growth processes may influence the emission dynamics during the course of a day.

Our measurements showed that during the most intensive elongation period, the Scots pine shoots grew during most of the day, but a pause or even mild shrinking was observed during the early morning hours (Fig. 6), potentially due to hydraulic limitations developing during the leaf development (Pantin et al., 2011). This had also a clear effect on the diurnal pattern of emissions during the needle elongation period (Figs. 5 and 7). Before and after the growth period (Fig. 7a–d and k–n) the average diurnal emission patterns and the daytime maxima were fairly similar in both mature and developing shoots, and the maximum emissions typically coincided with the daytime maximum temperatures. However, during the most intensive growth (Fig. 7f–i) the methanol, MBO and monoterpene emissions from growing shoots increased earlier in the morning, and reached the maximum emission rates earlier than emissions from the mature shoot. The difference in acetone emissions between growing and mature shoots was not as clear. Most importantly, the diurnal emission pattern of developing shoots did not match with the variations in temperature (Fig. 7j), contrary to that in mature shoots. After the maturation of needles in August the diurnal emission patterns between young and mature shoots did not differ from each other anymore (Fig. 7k–n), These results imply that there are other, more important drivers of emissions in growing shoots than temperature.

The diurnal pattern of terpenoid or other VOC biosynthesis has not been studied in detail, although reports on emission variations over the day abound. The observed significantly different diurnal pattern in emissions in growing and mature needles suggests that during the period of high metabolic activity, the biosynthesis of methanol, MBO and monoterpenes is indeed linked to the up-regulation of the respective pathways, and a potential circadian regulation of biosynthesis has been suggested (Laothawornkitkul et al., 2009).

Our results on the diurnal emission patterns are in line with Hewitt et al. (2011), who used micrometeorological methods in a tropical oil palm plantation and rain forest,

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and found out that isoprene emission potential had a very clear diurnal cycle with low night time and high daytime values with a maximum well before midday, contrary to the ambient temperature which reached the maximum somewhat later in the day. Isoprene is not stored in plant tissues, and therefore the biosynthesis also was most active in the morning hours. Our findings shed light on the results of Hewitt et al. (2011), providing a possible explanation for the high emission potential before noon.

4 Conclusions

In this study, we showed that the growing Scots pine shoots are emitting considerable amounts of volatile organic compounds. The needle elongation rate as well as timing of elongation correlated with the large VOC emissions, suggesting that growth processes and high emissions potentially have a causal relationship. Evidently the existing model approaches using only light and temperature as direct drivers for emissions are not able to capture the effect of growing foliar biomass on emissions. As the climate change – induced lengthening of growing season will most likely advance the timing of bud burst, the uncertainties in seasonal emission estimates related to plant growth may become even more important in the coming decades.

Based on our results, a refined, mechanistic description for emission processes during the new foliage biomass growth, as well as a more detailed description of the characteristic growth patterns for the different plant functional types should be implemented into emission models. In ecosystems where the timing of new foliar biomass differs from that found from boreal evergreen forests – where new needles grow within a time frame of about one hundred days – the effect of foliar biomass growth on VOC emissions is not necessarily confined to spring and early summer only. This calls upon a new generation of emission models, based on functions describing the drivers for key metabolic processes, and testing them under field conditions with datasets of sufficiently high temporal resolution.

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Our results bring new insights on the consequences of seasonality of biosphere activity and on the temporal variations in sources of aerosol precursor in forested ecosystems. We showed that during the three-four spring and summer months the monoterpene, methanol and MBO emissions are dominated by the new foliage growth. This may have considerable impact on the frequent springtime new particle formation events in boreal and temperate forests (Dal Maso et al., 2005; Manninen et al., 2010).

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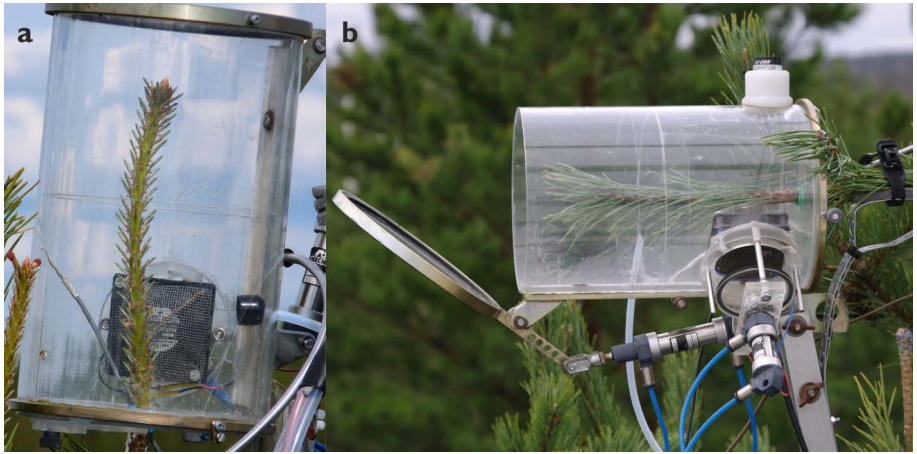

Fig. 1. Emission measurements with dynamic shoot enclosures. **(a)** The enclosure with a developing Scots pine shoot in the end of May, when the intensive needle elongation period begins. **(b)** The enclosure with a mature Scots pine shoot.

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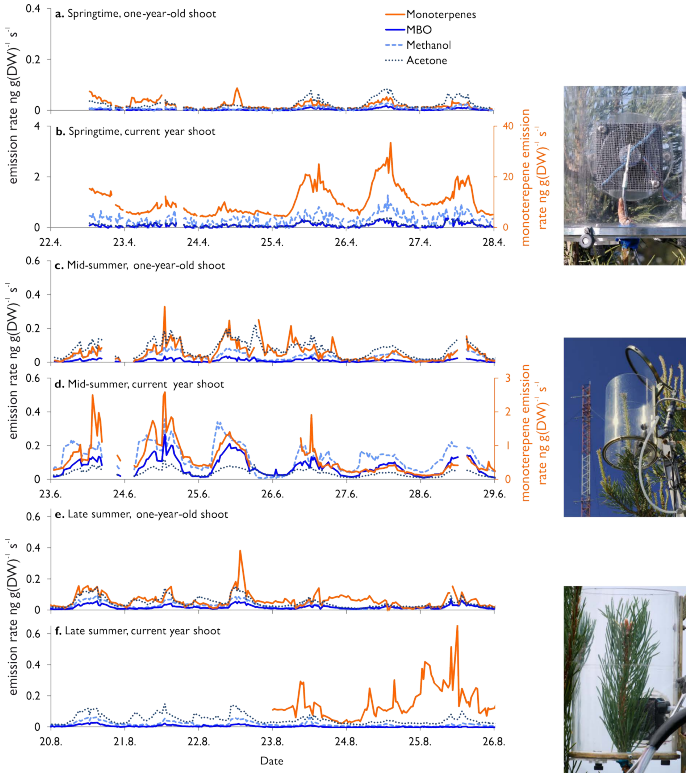

Fig. 2. Monoterpene, MBO and methanol emission rates from developing and mature Scots pine shoots. **(a, b)** 22–27 April 2010, during the dormancy break, before any growth commences. **(c, d)** 22–28 June 2010, during the most intensive needle elongation period. **(e, f)** 20–25 August 2010, the shoot length growth has ended. NOTE: In panels **(b)** and **(d)**, monoterpene emission rates of the current year bud/shoot are given in the right *y* axis due to magnitude differences in emission rates. Next to panels **(b)**, **(d)** and **(f)** photos from the corresponding stage of shoot development.

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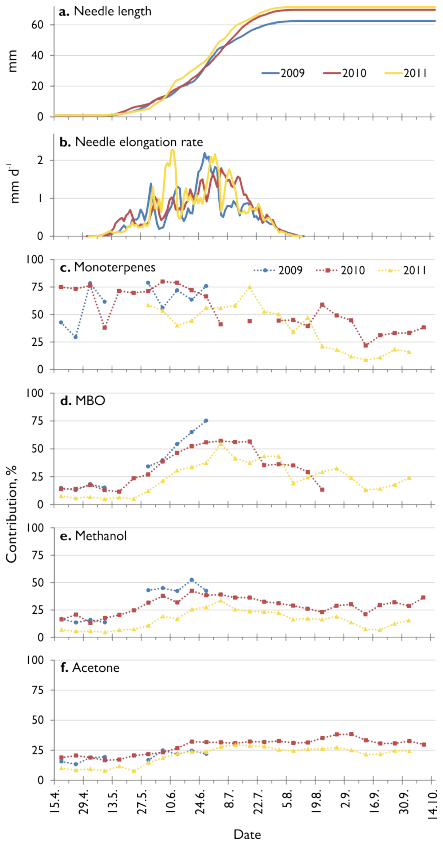

Fig. 3. The growth of needles and the relative contribution of developing shoot to the total foliage emissions. The points represent one week averages in three consecutive years (2009–2011). **(a)** Length of growing needles; **(b)** elongation rate of growing needles. The contribution of developing needle age class to total emissions of **(c)** monoterpenes, **(d)** MBO, **(e)** methanol, and **(f)** acetone.

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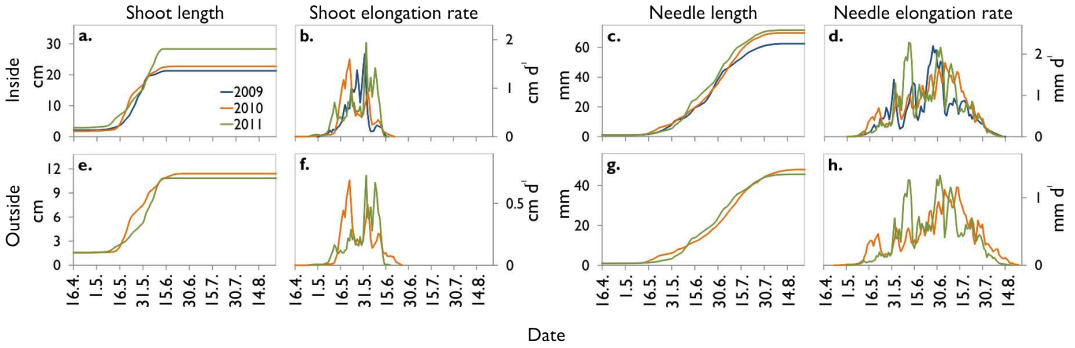

Fig. 4. The shoot and needle lengths and elongation rates during growing seasons 2009–2011. **(a–d)** Inside, **(e–h)** outside the shoot enclosure. The needle and shoot elongation outside the enclosure was not measured during the growing season 2009.

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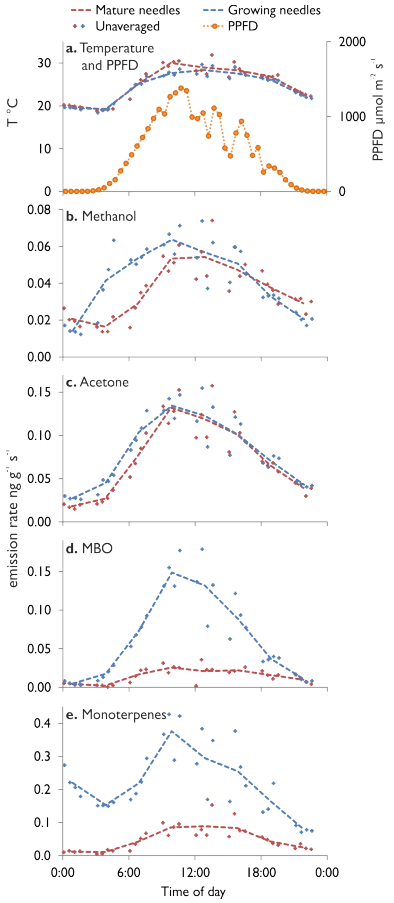

Fig. 5. The diurnal pattern in VOC emission rates from a mature and a developing Scots pine shoot on 8 July 2011. **(a)** Temperature inside enclosure and photosynthetic photon flux density. **(b–e)** Emission rates of different compounds. Crosses represent individual measurements, and dashed lines are three-hour averages.

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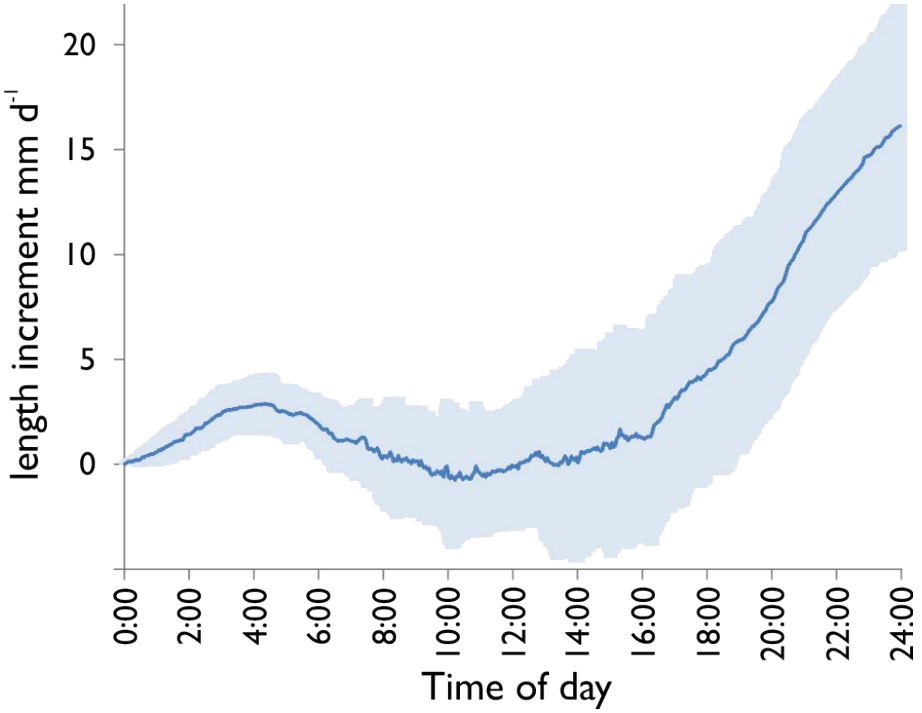

Fig. 6. The measured average shoot length increment diurnal pattern of a Scots pine shoot outside enclosure under unshaded conditions during 12 days with moderate elongation rate in summers 2010 and 2011. The shoot length in the beginning of day is set to 0. The shaded area represents ±1 standard deviation in shoot elongation.

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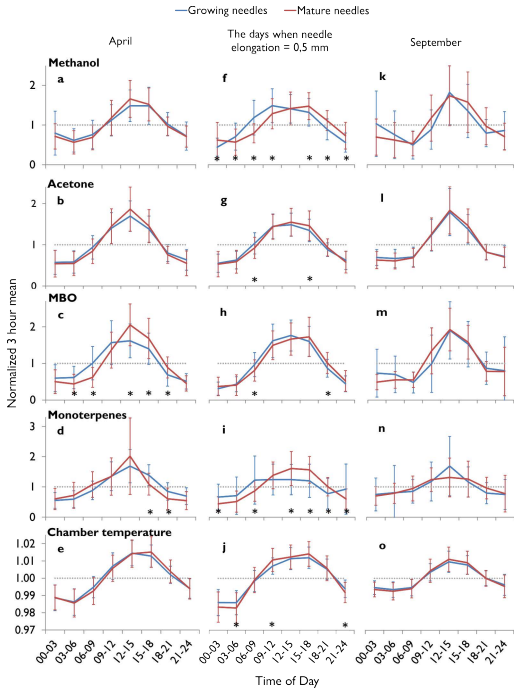

Fig. 7. The average diurnal cycle in VOC emissions from mature and developing Scots pine shoots during April before the onset of shoot growth **(a–d)**, in the most intensive needle elongation days (needle elongation $\geq 0.5\,\mathrm{mm\,d^{-1}}$, **(f–i)** and in September when growth has ended **(k–n)**. The *y* axis values are the 3 h average emission rates normalized to the average of each day. The grey dashed lines show the normalized daily averages (= 1). The error bars equal ±1 SD. The stars show statistically significant difference (*t* test, $p \leq 0.05$) in the normalized emissions between the developing and the mature shoot. The data is from years 2009–2011 (n = 11–67 days, mostly > 30 days). The three figures on the bottom (**e**, **j** and **o**) show the normalized average diurnal cycles in chamber temperatures during the corresponding days, calculated from the temperatures in Kelvin scale.

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