Biogeosciences, 9, 1291–1300, 2012
www.biogeosciences.net/9/1291/2012/
doi:10.5194/bg-9-1291-2012

Biogeosciences

Is forest management a significant source of monoterpenes into the boreal atmosphere?

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Received: 6 June 2011 – Published in Biogeosciences Discuss.: 10 August 2011
Revised: 8 March 2012 – Accepted: 14 March 2012 – Published: 10 April 2012

Abstract. Volatile organic compounds (VOCs) including terpenoids are emitted into the atmosphere from various natural sources. Damaging the plant tissue is known to strongly increase their monoterpene release. We measured the terpenoid emissions caused by timber felling, i.e. those from stumps and logging residue. The emissions from stumps were studied using enclosures and those from the whole felling area using an ecosystem-scale micrometeorological method, disjunct eddy accumulation (DEA). The compounds analyzed were isoprene, monoterpenes and sesquiterpenes. Strong emissions of monoterpenes were measured from both the stumps and from the whole felling area. The emission rate decreased rapidly within a few months after the logging. In addition to fresh logging residue, the results suggest also other strong monoterpene sources may be present in the felling area. These could include pre-existing litter, increased microbial activity and remaining undergrowth. In order to evaluate the possible importance of monoterpenes emitted annually from cut Scots pine forests in Finland, we conducted a rough upscaling calculation. The resulting monoterpene release was approximated to be on the order of 15 kilotonnes per year, which corresponds to about one tenth of the monoterpene release from intact forests in Finland.

1 Introduction

Biogenic volatile organic compounds (VOC) have many important effects on the atmosphere and climate. Although the emissions of biogenic VOCs in boreal areas have been studied quite intensively, large gaps still remain in our knowledge. In particular, the seasonality of the emission rates is poorly known (Rinne et al., 2009). Emission rates from Scots pine (*Pinus sylvestris*) have been measured throughout the growing season (Tarvainen et al., 2005) and there are few measurements from Norway spruce (*Picea abies*) also during dormant period (Hakola et al., 2003). These studies show that few biogenic VOCs are emitted during winter, and that these emission rates are low due to low temperatures (Tarvainen et al., 2005).

Mechanical damage to trees is known to enhance VOC emissions from, e.g. coniferous trees (Juuti et al., 1990; Litvak and Monson, 1998; Loreto at al., 2000) and birch species (Hakola et al., 2001). For coniferous trees this is expected to be particularly important as they store significant amounts of monoterpenes within their resin ducts. Since extensive forestry work is conducted during winter and spring months in boreal forests, cut stumps and logging residue can provide a source of VOCs into the atmosphere, possibly also during these biologically inactive periods. In winter, the lifetimes of VOCs are longer and are so possibly transported to a larger area. The spring is of great interest as the maximum aerosol particle formation events are observed at that time of year (Dal Maso et al., 2005), and is so expected to be strongly affected by VOCs in the atmosphere (Kulmala et al., 2004).

Strömvall and Petersson (1991) and Räisänen et al. (2008a) have reported clear increases in monoterpene concentration in air close to forestry work areas in boreal coniferous forests. Strömvall and Petersson (1991) measured up to 500 fold monoterpene concentration levels in air above fresh branch wood of Scots pine and Norway spruce compared to the background level. Räisänen et

al. (2008a) reported 2–3 fold concentration in air in a Scots pine clear-cut area for 7 weeks after the felling. During thinning of a ponderosa pine (*Pinus ponderosa*) plantation, tenfold monoterpene fluxes have been measured in California, USA (Schade and Goldstein, 2003). However, no long-term measurements of monoterpene emissions from cut forests have been reported to our knowledge.

The aim of the present study is to measure the VOC emission rates and composition from tree stumps and forest felling areas, their temporal evolution and dependency on environmental parameters. From the results we can evaluate the possible importance of VOC emissions originating from forestry work in comparison to intact ecosystems.

2 Materials and methods

2.1 Experimental sites and times

Measurements were carried out in southern Finland, close to the SMEAR II measurement station in Hyytiälä (61°51′ N, 24°17′ E, 180 m a.s.l). The area belongs to the southern boreal vegetation zone, with a mean annual temperature of about 3 °C and mean annual precipitation of about 700 mm. The emission rates and composition were measured in two forest stands after harvesting the merchantable stem wood. The slash, consisting of the branches and tree tops, was left at the sites without any treatment.

In 2007 the measurements were conducted on a clear-cut area of about 4.3 ha, felled in November 2006, which was dominated by Norway spruce. The emissions from single stumps of Norway spruce, Scots pine and birch (*Betula* spp.) were measured using enclosures. The same spruce stump was measured on four days in May, June and August 2007. The measurements were repeated one to four times per day, resulting in 11 samples. The emissions from a birch and a pine stump were measured twice on one day in June.

In 2008 we conducted a more extensive measurement campaign in a seed tree felling area of about 4.0 ha, felled in the end of April. In the seed tree method, around 50 trees per hectare (ca. 10 % of the original number on trees) had been left standing to advance the natural regeneration. The site was homogeneous, sowed Scots pine stand. Between May and September, the emissions of two Scots pine stumps were measured using enclosures. In addition to the stump emissions, the ecosystem scale emission was studied using a micrometeorological flux measurement method, disjunct eddy accumulation (Rinne at el., 2000), carried out on six days between June and September. To approximate the remaining biomass at the site, the total volume of merchantable wood and the mean stem volume were obtained from the timber company. Subsequently, the amount of needles, brushwood and roots were approximated using tabulated data (Marklund, 1988). The second column in Table 1 shows the estimated mass of each debris fraction at our study site. The third column lists the range of monoterpene content of each fraction based on literature (Manninen et al., 2002; Lin et al., 2007; Räisänen et al., 2008b; Isidorov et al., 2010). The given range reflects the variability of the content and thus the uncertainty of the estimate. The resulting range of monoterpene mass left behind at the site is listed in the last column. Using the same information, we also estimated the total cross sectional area of stumps per land area, resulting in around $0.003\,\mathrm{m^2_{SA}\,m^{-2}}$ (subscript SA referring to stump area).

2.2 Enclosure measurements

The enclosure measurements were carried out by placing a transparent Teflon bag around a tree stump. The bag was secured to the sides of the stump using tape. Air was pumped through the bag with a flow rate of about $4\,\mathrm{l\,min^{-1}}$. The inlet air was passed through a MnO_2 ozone scrubber. Most of the air pumped into the enclosure exited through the hemline of the bag. The chemical samples were taken from the inlet and the outlet ports to Tenax-TA/Carbopack-B adsorbent tubes with a constant flow rate of about $0.1\,\mathrm{l\,min^{-1}}$. The closure times varied between 30 min and 3 h. The emission rate from the stump was calculated from the concentration difference between the outlet and inlet airflow, and the flow rate through the enclosure. The emission rates were normalized to the cross sectional area of the stump ($\mathrm{m^2_{SA}}$). Temperature inside the enclosure and photosynthetic photon flux density (PPFD) outside the enclosure were recorded at the same time.

2.3 Disjunct eddy accumulator

The ecosystem scale emission flux was measured using the disjunct eddy accumulation (DEA) method (Rinne et al., 2000; Turnipseed et al., 2009). During the operation, a large primary sampling valve was opened once a minute for 200 ms. This allowed the pre-evacuated intermediate storage reservoir (V=1 l), made of electro-polished stainless steel, to fill with the sample air. Before sampling, the remaining pressure inside the intermediate storage reservoir was verified to be below 2 kPa. The vertical wind speed, measured with a sonic anemometer (Metek USA-1), placed above the accumulator at about 2 m above the ground, was recorded simultaneously. After sampling, air was drawn through one of the adsorbent tubes reserved for updraft and downdraft samples. The decision on which tube should be used was based on the direction of the vertical flow at the time of sampling. The volume of the adsorbent flow was proportional to the vertical wind velocity, resulting in a linearly proportional sample volume, and hence true eddy accumulation. The lines and valves downstream of the intermediate storage reservoirs were heated slightly above ambient temperature to avoid sticking of the VOCs on the instrument surfaces. Two similar samplers were operated simultaneously in turns resulting in 30 s sample intervals and altogether 110 samples during 55 min sampling periods. The flux calculation was

Table 1. The amount, estimated monoterpene content and the resulting monoterpene mass per land area of each of the debris fraction found in the seed tree felling area.

Fraction of the debris	Amount of the fraction in the area	Estimated monoterpene content in the fraction	Mass of monoterpenes in the fraction
needles	$280\,g_{dw}\,m^{-2}$	$2.5–8.0\,mg\,g_{dw}^{-1}$	$700–2240\,mg\,m^{-2}$
brushwood	$1000\,g_{dw}\,m^{-2}$	$1.0–1.6\,mg\,g_{dw}^{-1}$	$1000–1600\,mg\,m^{-2}$
roots	$1800\,g_{dw}\,m^{-2}$	$0.4–1.6\,mg\,g_{dw}^{-1}$	$720–2880\,mg\,m^{-2}$

conducted following the method derived for non-ideal conditions by Turnipseed et al. (2009). Continuous fetch extended to about 300 m upwind from the instrument location during the measurements.

2.4 Chemical analysis

All adsorbent samples were analyzed for isoprene, monoterpenes and sesquiterpenes in the laboratory using an automatic thermodesorption device (PerkinElmer TurboMatrix 650) connected to a gas chromatograph (PerkinElmer Clarus 600) with an Elite-1 column (60 m, i.d. 0.25 mm) and a mass-selective detector (PerkinElmer Clarus 600T). Detection limits for isoprene, monoterpenes and sesquiterpenes were $10\,ng\,m^{-3}$, $10–20\,ng\,m^{-3}$ and $20–50\,ng\,m^{-3}$, respectively. Of the monoterpenes α-pinene, camphene, β-pinene, Δ^3-carene, limonene, 1,8-cineol and terpinolene and of the sesquiterpenes copaene, longicyclene, isolongifolene, longifolene, β-caryophyllene, aromadendrene, α-humulene and alloaromdendrene were measured. No breakthrough was detected for any of the compounds from Tenax-TA/Carbopack-B tubes when sampling for 3 h with the flow rate of about $0.1\,l\,min^{-1}$. The overall uncertainties of sampling and analysis, calculated from parallel samples, were 12 %, 10…40 % and 33…52 % for isoprene, monoterpenes and sesquiterpenes, respectively.

3 Results and discussion

3.1 Emissions from stumps

Both spruce and pine stumps measured in 2007 emitted large amounts of monoterpenes and some sesquiterpenes. The average monoterpene emission from spruce and pine stumps were $5100\,\mu g\,m_{SA}^{-2}\,h^{-1}$ and $52\,000\,\mu g\,m_{SA}^{-2}\,h^{-1}$, respectively. For the spruce stump, the monoterpene emission rate remained almost constant for the whole summer and it was weakly dependent on temperature. The monoterpene emission was dominated by α-pinene (67 %) and β-pinene (20 %). The sesquiterpene emission rate increased in August compared to the measurements earlier in summer. In August the sesquiterpene contribution was about 4 % of that of monoterpene emissions. Earlier, in May and June it was only less than 1 %. Hakola et al. (2003) measured the emission rates from living Norway spruce and they found that the contribution of sesquiterpenes was rather small compared to monoterpene emission rates early summer, while in July these emissions increased, contributing more than monoterpenes to the total VOC emission.

In 2008 we measured the emission from a pine stump several times, beginning 3 weeks after logging. The average mono- and sesquiterpene emissions from the pine stumps were $25\,000\,\mu g\,m_{SA}^{-2}\,h^{-1}$ and $600\,\mu g\,m_{SA}^{-2}\,h^{-1}$, respectively. The emission rates of both mono- and sesquiterpenes were weakly dependent on temperature. The monoterpene emission spectra of the two pine stumps studied in 2008 are plotted in Fig. 1. There is a clear difference between the two studied stumps: one emits mainly α-pinene (77 %) and the other mainly Δ^3-carene (79 %). There are different Scots pine genotypes growing in Finland, known to have differences in the monoterpene composition (e.g. Tarvainen et al., 2005 and the references therein; Bäck et al., 2012). The stumps studied in our campaign were clearly of different genotypes, which explain the observed difference in their VOC blend.

The monoterpene emission from the birch stump was orders of magnitude lower than from the studied conifers, the average monoterpene emission being $40\,\mu g\,m_{SA}^{-2}\,h^{-1}$. It emitted mainly α-pinene, β-pinene, limonene and camphene. Sesquiterpene emission from the birch stump was negligible. It was not possible to identify whether the stump was silver or downy birch. Both of these birch species are known to have variable mono- and sesquiterpene emissions from their leaves (Hakola et al., 2001; Vuorinen et al., 2005). The emissions from the wooden parts (stem, bark) have not been reported. However, as birches do not have resin ducts or other large storage structures for terpenoids and the emission is entirely of de novo origin (Klika et al., 2004; Baser and Bemirci 2007; Ghirardo et al., 2010), the emission from woody parts is likely to be very small. Thus, it is easy to understand that the emissions were very small after the trees were cut down.

3.2 Ecosystem scale emissions

The ecosystem scale emissions were measured on 6 days between 13 June and 17 September 2008. Altogether, 30 one-hour periods were measured. The measured monoterpene

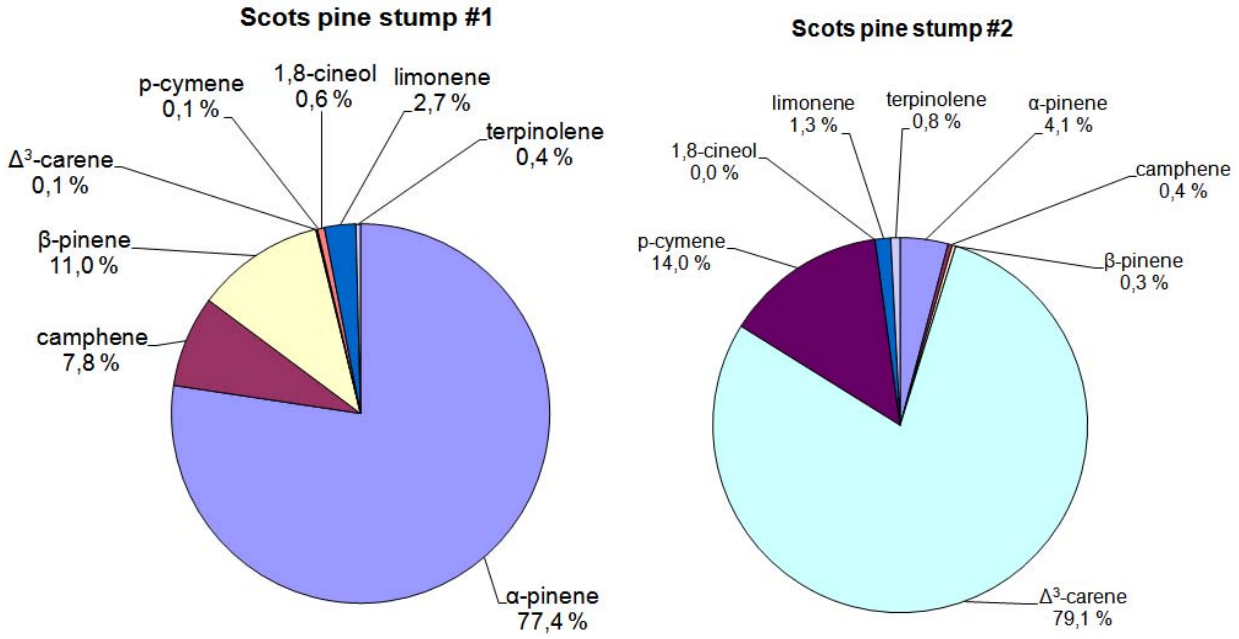

Fig. 1. The monoterpene emission spectra of the two individual Scots pine stumps.

fluxes are shown in Fig. 2. The wind data from the first measurement day, 13 June 2008, were probably contaminated from horizontal wind components due to a tilted mast. This was indicated by the large positive values of the mean vertical wind velocity (up to $1.8\,\mathrm{m\,s^{-1}}$). Since air sampling is controlled on-line by the wind measurement, no post-processing corrections were possible and all data from that day were discarded from further analyses. However, we show these discarded data in the Figs. 2 and 3 as an order of magnitude estimate. Relative uncertainty of the flux was estimated using analytical uncertainties of the samples and an uncertainty estimate of the wind measurements. For the sum of monoterpenes, the uncertainty of a single flux value was about 21 %. Additional statistical uncertainty in the fluxes due to disjunct sampling was estimated to be σ_{m}=9.55$(1000\frac{\Delta t}{T_{\mathrm{avg}}})^{0.5}$ = 29 % as given by the expression derived from Turnipsseed et al. (2009). Although we do not know the exact distribution of the errors, they are independent and add up to about 36 % total uncertainty.

High emission of monoterpenes was detected at the beginning of the campaign, with the highest measured value being about $5200\,\mu\mathrm{g\,m^{-2}\,h^{-1}}$. Schade and Goldstein (2003) measured up to about $3800\,\mu\mathrm{g\,m^{-2}\,h^{-1}}$ monoterpene fluxes during and after ponderosa pine thinning, which is in line with our results. The measured fluxes exhibit large hour to hour variations. This may be explained not only by random error, but also by great patchiness of the source area. As the footprint area changes with wind and stability, the amount of emission hot spots captured by the measurement system changes. Therefore, the further analyses are based only on daily averages. The emissions were dominated by monoterpenes α-pinene and Δ^3-carene with minor contributions from ß-pinene and camphene. Although some emission of sesquiterpenes was measured from the stumps using enclosures, in the ecosystem scale these were not detected. Concentrations and fluxes of sesquiterpenes are difficult to measure at ecosystem scale as they react rapidly in air, already below the measurement height, and sesquiterpenes reaching the measurement equipment are easily destroyed inside the system, e.g. by rapid reactions with the ozone (e.g. Helmig et al., 2004 and the references therein).

In Fig. 3 we show the temporal evolution of the fluxes together with corresponding air temperatures. The flux values shown are the averages of the fluxes measured on a particular day together with temperatures averaged over the same time period. A pronounced feature of this time series is a rapid decrease of the monoterpene emission rate during the summer. From Fig. 3 it is apparent that the flux from the felled area does not follow primarily temperature. This, we would expect to be the case if the emissions originated from evaporation of constant monoterpene reservoirs, or from living vegetation. Therefore, we may assume that the majority of the emissions originate from logging residue that has limited reservoirs with collapsing pathways to the atmosphere. It is impossible to determine the short-term temperature dependency of the emissions from the present dataset, as the temperature variation during one measurement day was very small.

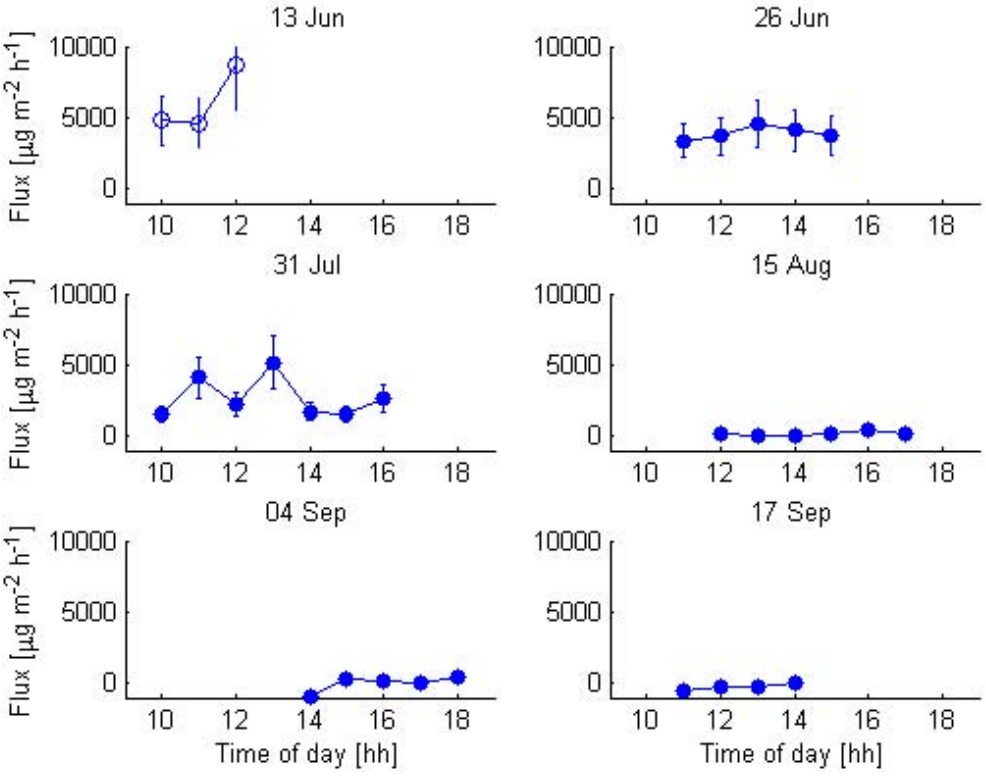

Fig. 2. Ecosystem scale monoterpene fluxes measured using disjunct eddy accumulation (DEA) between 13 June and 17 September, 2008. The data from 13 June were discarded from further analyses due to corrupted wind measurement and are shown here by open circles.

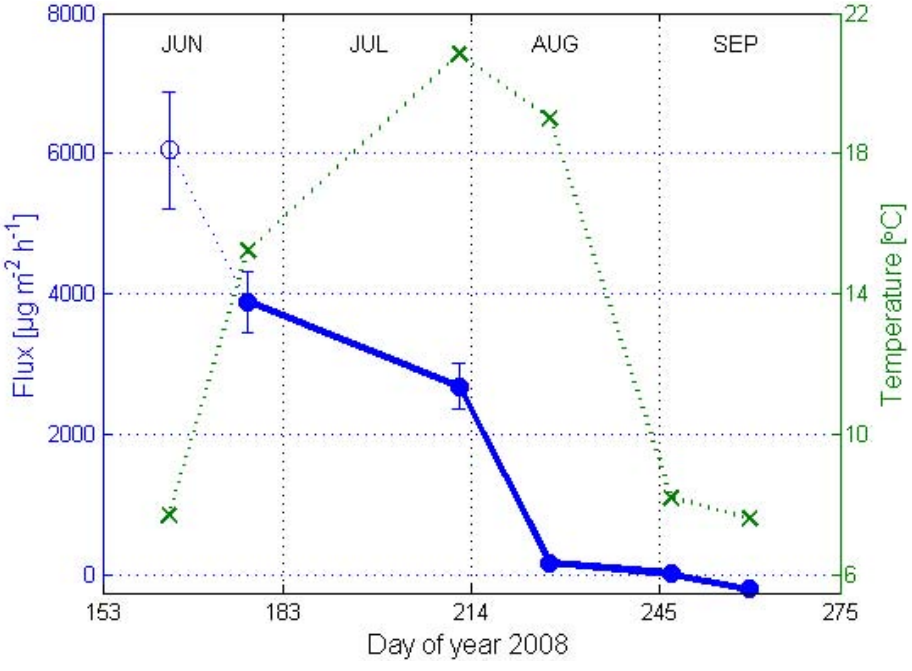

Fig. 3. Daily mean fluxes of monoterpenes (blue solid line) and corresponding air temperatures (dotted green line). Error bars of the fluxes are the standard errors of the means. The data of 13 June were discarded from further analyses due to corrupted wind measurement and are shown here by open circle.

In addition to the logging residue, ground vegetation and soil may also emit monoterpenes. Hellén et al. (2006) reported monoterpene emissions up to 373 µg m^{-2} h^{-1} from natural forest floor at the nearby SMEAR II measurement station. Their measurement plot included mosses, shrubs, and some litter, originating mainly from Scots pine and undergrowth. Hayward et al. (2001) measured somewhat lower monoterpene emission from undisturbed soil in a Sitka spruce (*Picea sitchensis*) forest in UK. However, they reported a significant increase in the emissions when the topmost layers (∼3 cm) were removed to expose some fine roots. Isidorov et al. (2010) reported significant monoterpene emissions from needle litter of Scots pine (up to 7.5 µg g_{dw}^{-1} h^{-1}) and Norway spruce (up to 1.5 µg g_{dw}^{-1} h^{-1}) for about six months after the beginning of their decay. Asensio et al. (2008) found significant amounts of monoterpenes and sesquiterpenes in the litter, soil and roots close to Aleppo pine (*Pinus halepensis*) trees. The ground vegetation and root systems remaining suffer heavy mechanical damage during felling operations, which may increase their monoterpene emissions.

After the forest felling, the remaining ground vegetation and soil encounter several stress factors due to changes in the environment: solar radiation increases heavily, temperature rise while its diurnal variability becomes larger, water balance changes, and more nutrients become available. Besides, the damaged soil surface exposes fine roots and partially decayed litter to atmospheric conditions. Increased terpenoid emissions are a fundamental response of plants to environmental stresses (e.g. Loreto and Schnitzler, 2010; Niinemets, 2010). Therefore, it can be considered likely that the monoterpene emissions from ground vegetation and preexisting decaying litter rises substantially as a consequence of forest felling.

3.3 Temporal evolution of emission rates

In order to get comparable emission rates to estimate the temporal evolution of the emissions and to further upscale the results, we normalized the emissions to +15 °C using equation

$$\mathrm{E} = \exp\left(\frac{-b}{T+a}\right), \quad (1)$$

where b = 5400 K, based on the temperature dependency of monoterpene saturation vapor pressure. Figure 4a and b shows the temperature compensated emissions of both of the stumps and the whole ecosystem, calculated from the daily average emissions. Note that the stump emission is given per stump cross sectional area (m^2_{SA}) and the ecosystem emission per land area (m^2). In order to upscale, the measured emission potentials were interpolated and extrapolated to yield a continuous emission rate estimate over the whole growing season. We extrapolated the emission potentials two to seven weeks backwards and six weeks forwards as compared to the period covered by the measurement data.

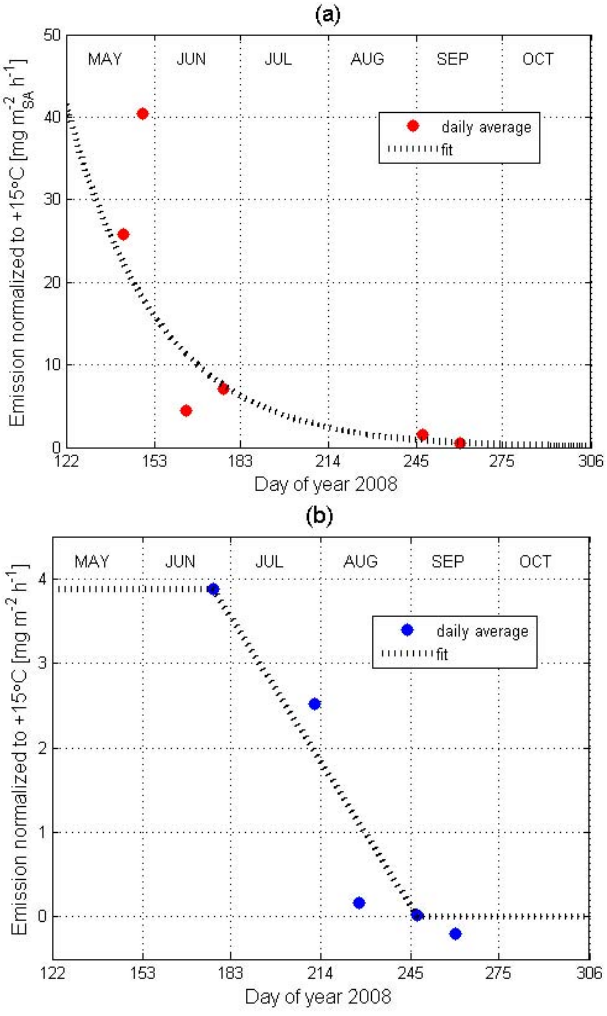

Fig. 4. The monoterpene emissions normalized to +15 °C calculated from the daily averaged emission measurements. **(a)** Red dots are the emissions from the Scots pine stump and the dotted black line the fit used in the upscaling. **(b)** Blue dots are the ecosystem scale emissions and the dotted black line is the fit used in the upscaling. See text for details of the fitted lines.

The Scots pine stump emission E_S is modeled as an exponential decay of the form

$$E_S = 1821.7 \text{ mg m}^2_{SA} \text{ h}^{-1} \times e^{0{,}021D}, \quad (2)$$

where D is the day of the year. This a best-fit curve to the data with R^2=0.86.

The ecosystem scale emission E is modeled piecewise by three lines:

(i) a constant part $E = 3.88$ mg m^{-2} h^{-1}, (3)

covering days 122…177;

(ii) decaying regression of the form (4)

$$E = -0.0551 \frac{\text{mg m}^{-2} \text{ h}^{-1}}{d} D + 13.64 \text{ mg m}^{-2} \text{ h}^{-1},$$

covering days 178...247 and

(iii) a constant part $E = 0\ \mathrm{mg\ m^{-2}\ h^{-1}}$, (5)

covering days 248...305. Here, we assumed a constant value before the first and after the last measurement point, and fitted a straight line between these. Due to exiguity of data points, this simple and conservative approach was chosen. Both stump and ecosystem emissions show a clear decaying trend in the emission rate. During the first months the emission rate decreased rapidly, with a slower decrease towards zero around four months after the logging. During the first month after logging, fresh resin appeared on the stump surface, probably causing the high emission.

3.4 Estimate of the total monoterpene release and upscaling

To estimate the total monoterpene release from the felled forest stand, the Scots pine stump emissions and those in ecosystem scale were calculated using the normalized emission curves (Eqs. (2–5); Fig. 4) derived in the present study. For comparison, we calculated the monoterpene emissions from an intact Scots pine forest stand using a temperature dependent emission algorithm (Guenther et al., 1993) and the constant emission potential E_0=1.24 $\mathrm{mg\,m^{-2}\,h^{-1}}$, derived from the measurement data from the SMEAR II station (Rinne et al., 2007). The estimate was done for May-October 2008, which roughly corresponds to growing season in southern Finland. To run the algorithms we used the air temperature measured at the height of 8.4 m (within the forest trunk space) at SMEAR II station in Hyytiälä in 2008. To give an overview of the weather conditions during the studied period, we plotted daily minima and maxima temperatures in Fig. 5a. The growing season of 2008 was characterized by a warm spell in the beginning of May followed by a short cold period. The mean temperature during the high emission season (May, June, July) was 12.3 °C with a standard deviation of 4.3 °C. The observed mean temperature is close to 15 °C, which was used as a normal temperature throughout this study.

Using the data described above, the emissions were calculated for every half-hour period. Daily sums of monoterpene emission were calculated from the half-hourly emission data, and plotted as the cumulative monoterpene release in Fig. 5b. Over the whole six month period, the resulting ecosystem scale monoterpene releases from the cut and intact forests were about 8.5 $\mathrm{g\,m^{-2}}$ and 1.0 $\mathrm{g\,m^{-2}}$, respectively. The emission from the stumps alone was 33 $\mathrm{g\,m_{SA}^{-2}}$. Using the stump coverage of 0.003 $\mathrm{m_{SA}^2\ m^{-2}}$, this corresponds to about 0.1 $\mathrm{g\,m^{-2}}$ at the stand scale.

To evaluate the plausibility of our results, we compared the total monoterpene release calculated above to the initial monoterpene content of logging debris. Table 1 shows the estimated mass of each debris fraction at our study site, the range of monoterpene content of each fraction found in the literature (Manninen et al., 2002; Lin et al., 2007; Räisänen et al., 2008b; Isidorov et al., 2010), as well as the resulting range of monoterpene release, given that all the monoterpenes evaporated. The total monoterpene content of the logging debris falls within the range of 2.4–6.7 $\mathrm{g\,m^{-2}}$, which is somewhat lower than the total monoterpene release of 8.5 $\mathrm{g\,m^{-2}}$ obtained in the present study. Moreover, it can be considered unlikely that all of the stored monoterpenes, including those from the roots, evaporated during the first couple of months after the logging. Therefore, there appears to be a discrepancy in our results compared to what we could expect based on previously published monoterpene contents.

A discrepancy of the same kind can be found in the data of Isidorov et al. (2010) and it is briefly discussed by the authors (Interactive comment on Biogeosciences Discuss., 7, 1727,

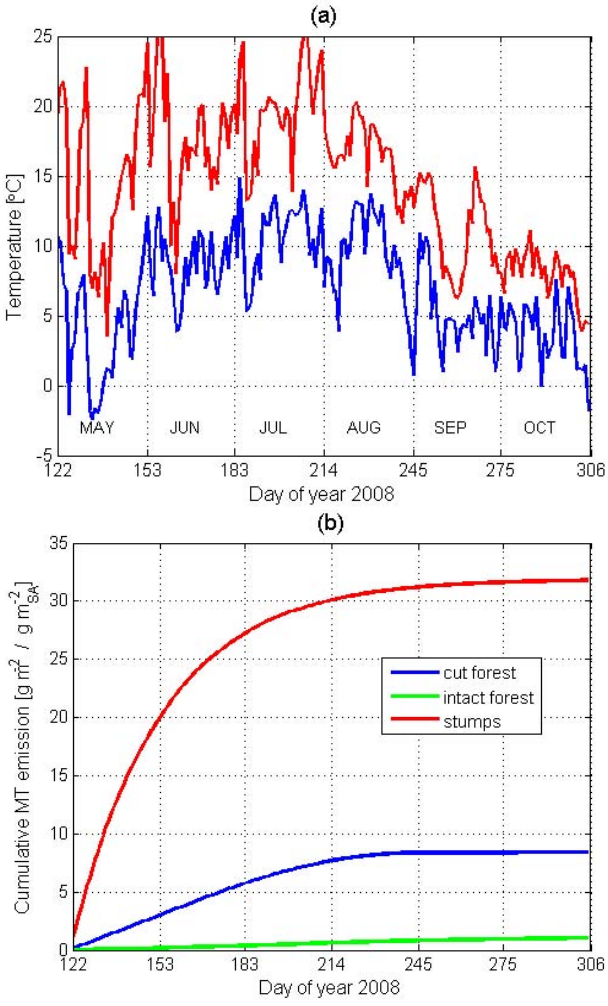

Fig. 5. (a) Daily minima (blue) and maxima (red) of the temperature data used in the upscaling. **(b)** Cumulative monoterpene emissions from the cut Scots pine forest (blue), intact Scots pine forest (green), and from Scots pine stumps alone (red). Note that the last one is given per stump area instead of land area.

2010). In their litter bag experiment studying decomposing needles of Scots pine, they observed monoterpene mass to decrease from 2533 $\mu g\, g_{dw}^{-1}$ to 2475 $\mu g\, g_{dw}^{-1}$ during the 77 first days of the experiment. At the same time, the emission rate measurements suggested up to 3500 $\mu g\, g_{dw}^{-1}$ monoterpene release. They explain the estimated cumulative monoterpene emission exceeding the initial monoterpene content of the needles by the temperature conditions during their experiment. They conducted their emission measurements in a laboratory at a temperature of about 20 °C. Between measurements, samples were stored in soil where the temperature varied around 0 °C, thus, slowing down the monoterpene release. However, this discrepancy is not fully explained, assuming the temperature dependency of monoterpene release from litter to be even close to that observed for living plants (Guenther et al., 1993) or that obtained from monoterpene saturation vapor pressure. Furthermore, they speculate that hydrolysis of bound terpenes may release new terpenes to be emitted from the litter, and that decomposing fungi may maintain the terpene emission.

Based on these observations it can be speculated that microorganisms may have an important role in the production of monoterpenes from litter. This assumption is supported by literature demonstrating growth condition-dependent (Nilsson et al., 1996) and species-dependent (Bäck et al., 2010) monoterpene emissions from isolated fungi. Furthermore, real litter samples are known to emit monoterpenes (e.g. Leff and Fierer, 2008), also from deciduous leaves litter that did not contain monoterpenes originally (Isidorov and Jdanova, 2002).

In order to estimate the significance of forest management to the total monoterpene emission in Finland, we conducted a simple upscaling. To estimate the total amount of monoterpenes emitted annually due to forestry operations from Scots pine forests in Finland, we upscaled this to cover all cutting methods. Instead of area, we used harvested volume as a scaling factor, as the emissions are expected to be dependent on the amount of felling waste rather than on the treated area. Furthermore, the statistics on the harvested volume are very reliable and easily available. In the seed tree felling area where our measurements were conducted, the drain of the merchantable wood was 135 $m^3\, ha^{-1}$. Since the monoterpene emission for the six month period was calculated to be about 8.5 $g\, m^{-2}$, this yields a monoterpene release of about 630 $g\, m^{-3}$. According to the cutting statistics from 1998–2007 (Finnish Forest Research Institute, 2008), the total annual drain of Scots pine trees from Finnish forests is about 24 000 000 m^3, which leads to a monoterpene release of about 15 kilotonnes per year. The total annual emissions of monoterpenes from intact forests in Finland are estimated to be about 114 kilotonnes (Tarvainen et al., 2007). In that inventory, the reduction of biomass in cut areas is indirectly taken into account – leading to reduction of emission. However, as the area cut annually is small, this effect is also minimal. Surprisingly, the monoterpene emissions caused by forestry operations in Scots pine forests seem to be as high as one tenth of the natural emission. Somewhat lower figures may be assumed for Norway spruce forests in Finland, since their drain is similar to Scots pines, but monoterpene content is smaller.

We calculated the annual cross sectional area of the new Scots pine stumps separately for different logging methods. The calculation is based on the drain (Finnish Forest Research Institute, 2008) and estimated average tree forms for each method. The emissions from stumps alone appear to be of minor importance, since the total cross sectional area of new stumps of Scots pines are about 500 ha per year. Using the above derived release of 33 $g\, m_{SA}^{-2}$, the total monoterpene release would be 0.2 kilotonnes per year, which is only about 1 % of the total ecosystem emission.

Our results suggest as high as 10 % increase to the total monoterpene release into the atmosphere as compared to previous inventories. There is some evidence that the observed concentrations of monoterpenes in the air are not fully explained by known biogenic emissions (Lappalainen et al., 2009). Although our measurement data is very limited, it provides evidence that forestry-induced emissions of monoterpenes may be of great importance for the air chemistry in certain areas. Obviously, more measurement data and model development are needed in order to reliably quantify the VOC emissions resulting from forest management.

4 Conclusions

Large monoterpene emissions were measured from both single stumps and from the whole felling area. The emissions of sesquiterpenes were small and the emissions of isoprene were negligible. In the present study only a very limited dataset was collected. A small dataset leads to large uncertainty, particularly regarding upscaling. The exact result depends heavily on extrapolation and interpolation of normalized emissions. We chose a rather conservative way in the extrapolation. Despite large uncertainties we believe that the order of magnitude of our upscaled result presented is reliable and our conclusion on the importance of the forest management to the aerial concentration of monoterpenes is justified.

The present study gives some hints that, e.g. increased microbial processes in litter or soil, may significantly increase the monoterpene emissions from forest felling area. This effect may be so large that the total monoterpene release during six months exceeds the original monoterpene content of the logging residue left on-site. Some support for this finding can also be found in the literature. However, further specific studies with carefully designed experiments are needed to verify and properly quantify this effect.

In any case, the amount of the monoterpenes emitted due to forestry operations is significant. In addition to changing the amount of monoterpenes emitted into the atmosphere,

forestry work may also alter the timing of the emissions over the year. Forestry work conducted in the wintertime could provide a source of VOCs into the atmosphere also during this biologically inactive period. Although the emissions from logging waste should be smaller in the wintertime due to low temperatures and snow cover, at the same time, the longer lifetime in the atmosphere may increase the importance of these emissions.

Acknowledgements. We thank P. Teittinen and Metsähallitus (Finnish Forest and Park Service) for allowing us to use their lands for the measurements. S. Haapanala acknowledges Maj and Tor Nessling Foundation for financial support. This research was supported by the Academy of Finland Center of Excellence program (project number 1118615).

Edited by: C. Spirig

References

Asensio, D., Owen, S. M., Llusià, J., and Peñuelas, J.: The distribution of volatile isoprenoids in the soil horizons around Pinus halepensis trees, Soil Biol. Biochem., 40, 2937–2947, 2008.

Başer, K. H. C. and Demirci, B.: Studies on Betula essential oils, ARKIVOC, vii, 355-348, 2007.

Bäck, J., Aaltonen, H., Hellén, H., Kajos, M., Patokoski, J., Taipale, R., Pumpanen, J., and Heinonsalo, J.: Variable emissions of microbial volatile organic compounds (MVOCs) from root-associated fungi isolated from Scots pine, Atmos. Environ., 44, 3651–3659, 2010.

Bäck, J., Aalto, J., Henriksson, M., Hakola, H., He, Q., and Boy, M.: Chemodiversity of a Scots pine stand and implications for terpene air concentrations, Biogeosciences, 9, 689–702, doi:10.5194/bg-9-689-2012, 2012

Dal Maso, M., Kulmala, M., Riipinen, I., Wagner, R., Hussein, T., Aalto, P. P., and Lehtinen, K. E. J.: Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland, Boreal Env. Res., 5, 323–336, 2005.

Finnish Statistical Yearbook of Forestry 2008, Finnish Forest Research Institute, Vantaa, Finland, ISBN 978-951-40-2131-2, 2008.

Ghirardo, A., Koch, K., Taipale, R., Zimmer, I., Schnitzler, J.-P., and Rinne, J.: Determination of de novo and pool emissions of terpenes from four common boreal/alpine trees by $^{13}CO_2$ labelling and PTR-MS analysis, Plant Cell Environ., 33, 781–792, 2010.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and Monoterpene Emission Rate Variability: Model Evaluations and Sensitivity Analyses, J. Geophys. Res., 98, 12609–12617, 1993.

Hakola, H., Laurila, T., Lindfors, V., Hellén, H., Gaman, A., and Rinne, J.: Variation of the VOC emission rates of birch species during the growing season, Boreal. Env. Res., 6, 237–249, 2001.

Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellén, H., and Keronen, P.: Seasonal variation of VOC concentrations above a boreal coniferous forest, Atmos. Environ., 37, 1623–1634, 2003.

Hayward, S., Muncey, R. J., James, A. E., Halsall, C. J., and Hewitt, C. N.: Monoterpene emissions from soil in a Sitka spruce forest, Atmos. Environ., 35, 4081–4087, 2001.

Hellén, H., Hakola, H., Pystynen, K.-H., Rinne, J., and Haapanala, S.: C_2-C_{10} hydrocarbon emissions from a boreal wetland and forest floor, Biogeosciences, 3, 167–174, doi:10.5194/bg-3-167-2006, 2006.

Helmig, D., Bocquet, F., Pollmann, J., and Revermann, T.: Analytical techniques for sesquiterpene emission rate studies in vegetation enclosure experiments, Atmos. Environ., 38, 557–572, 2004.

Isidorov, V. and Jdanova, M.: Volatile organic compounds from leaves litter, Chemosphere, 48, 975–979, 2002.

Isidorov, V. A., Smolewska, M., Purzyńska-Pugacewicz, A., and Tyszkiewicz, Z.: Chemical composition of volatile and extractive compounds of pine and spruce leaf litter in the initial stages of decomposition, Biogeosciences, 7, 2785–2794, doi:10.5194/bg-7-2785-2010, 2010.

Juuti, S., Arey, J., and Atkinson, R.: Monoterpene Emission Rate Measurements From a Monterey Pine, J. Geophys. Res., 95, 7515–7519, 1990.

Klika, K. D., Demirci, B., Salminen, J.-P., Ovcharenko, V. V., Vuorela, S., Can Başer, K. H., and Pihlaja, K.: New, sesquiterpene-type bicyclic compounds from the buds of Betula pubescens – ring-contracted products of β-caryophyllene? Eur. J. Org. Chem., 2004, 2627–2635, 2004.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, 2004.

Lappalainen, H. K., Sevanto, S., Bäck, J., Ruuskanen, T. M., Kolari, P., Taipale, R., Rinne, J., Kulmala, M., and Hari, P.: Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors, Atmos. Chem. Phys., 9, 5447–5459, doi:10.5194/acp-9-5447-2009, 2009.

Leff, J. W. and Fierer, N.: Volatile organic compound (VOC) emissions from soil and litter samples, Soil Biol. Biochem., 40, 1629–1636, 2008.

Lin, C., Owen, S. M., and Peñuelas, J.: Volatile organic compounds in the roots and rhizosphere of Pinus spp., Soil Biol. Biochem., 39, 951–960, 2007.

Litvak, M. E. and Monson, R. K.: Patterns of induced and constitutive monoterpene production in conifer needles in relation to insect herbivory, Oecologia, 114, 531–540, 1998.

Loreto, F. and Schnitzler, J.-P.: Abiotic stresses and induced BVOCs, Trends Plant Sci., 15, 154–166, 2010.

Loreto, F., Nascetti, P., Graverini, A., and Mannozzi, M.: Emission and content of monoterpenes in intact and wounded needles of the Mediterranean pine, Pinus pinea, Funct. Ecol., 14, 589–595, 2000.

Manninen, A.-M., Tarhanen, S., Vuorinen, M., and Kainulainen, P.: Comparing the variation of needle and wood terpenoids in Scots pine provenances, J. Chem. Ecol., 28, 211–228, 2002.

Marklund, L. G.: Biomass functions for pine, spruce and birch in Sweden, Department of Forest Survey, Report 45, Swedish University of Agricultural Sciences, ISBN 91-576-3524-2, 1988.

Niinemets, U.: Mild versus severe stress and BVOCs: thresholds, priming and consequences, Trends Plant Sci., 15, 145–153, 2010.

Nilsson, T., Larsen, T. O., Montanarella, L., and Madsen, J. Ø.: Application of head-space solid-phase microextraction for the analysis of volatile metabolites emitted by Penicillium species, J. Microbiol. Meth., 25, 245–255, 1996.

Rinne, J., Delany, A., Greenberg, J., and Guenther, A.: A true eddy accumulation system for trace gas fluxes using disjunct eddy sampling method, J. Geophys. Res., 105, 24791–24798, 2000.

Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T. M., Hellén, H., Kajos, M. K., Vesala, T., and Kulmala, M.: Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling, Atmos. Chem. Phys., 7, 3361–3372, doi:10.5194/acp-7-3361-2007, 2007.

Rinne, J., Bäck, J., and Hakola, H.: Biogenic volatile organic compound emissions from Eurasian taiga: Current knowledge and future directions, Boreal Environ. Res., 14, 807–826, 2009.

Räisänen, T., Ryyppö, A., and Kellomäki, S.: Impact of timber felling on the ambient monoterpene concentration of a Scots pine (Pinus sylvestris L.) forest, Atmos. Environ., 42, 6759–6766, 2008a.

Räisänen, T., Ryyppö, A., Julkunen-Tiitto, R., and Kellomäki, S.: Effects of elevated CO_2 and temperature on secondary compounds in the needles of Scots pine (Pinus sylvestris L.), Trees, 22, 121–135, 2008b.

Schade, G. W. and Goldstein, A. H.: Increase of monoterpene emissions from a pine plantation as a result of mechanical disturbances, Geophys. Res. Lett., 30, 1380, doi:1310.1029/2002GL016138, 2003.

Strömvall, A.-M. and Petersson, G.: Conifer monoterpenes emitted to air by logging operations Scand, J. Forest Res., 6, 253–258, 1991.

Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., and Kulmala, M.: Temperature and light dependence of the VOC emissions of Scots pine, Atmos. Chem. Phys., 5, 989–998, doi:10.5194/acp-5-989-2005, 2005.

Tarvainen, V., Hakola, H., Rinne, J., Hellén, H., and Haapanala, S.: Towards a comprehensive emission inventory of terpenoids from boreal ecosystems, Tellus, 54B, 526–534, 2007.

Turnipseed, A. A., Pressley, S. N., Karl, T., Lamb, B., Nemitz, E., Allwine, E., Cooper, W. A., Shertz, S., and Guenther, A. B.: The use of disjunct eddy sampling methods for the determination of ecosystem level fluxes of trace gases, Atmos. Chem. Phys., 9, 981–994, doi:10.5194/acp-9-981-2009, 2009.

Vuorinen, T., Nerg, A.-M., Vapaavuori, E., and Holopainen, J.: Emission of volatile organic compounds from two silver birch (Betula pendula Roth) clones grown under ambient and elevated CO_2 and different O_3 concentrations, Atmos. Environ., 39, 1185–1197, 2005.