Spruce bark beetles (*Ips typographus*) cause up to 700 times higher bark BVOC emission rates compared to healthy Norway spruce (*Picea abies*)

Erica Jaakkola[1], Antje Gärtner[1], Anna Maria Jönsson[1], Karl Ljung[2] Per-Ola Olsson[1], Thomas Holst[1]

[1]Department of Physical Geography and Ecosystem Science, Lund University, Lund, 223 62, Sweden
[2]Department of Geology, Lund University, Lund, 223 62, Sweden

Correspondence to: Erica Jaakkola (erica.jaakkola@nateko.lu.se)

Abstract

Emissions of biogenic volatile organic compound (BVOC) from the bark of Norway spruce (*Picea abies*) trees can be affected by stress, such as infestation of spruce bark beetles (*Ips typographus*). The difference in emission rates between healthy and infested Norway spruce bark was studied, as well as the influence of time since spruce bark beetle infestation started and the difference in emission rates from bark beetle drilled entry and exit holes. Bark chamber measurements on both healthy and infested trees were performed during the summer of 2019 at Hyltemossa and Norunda research station in Sweden. To consider the seasonal pattern of the spruce bark beetle, the emission rates from infested trees were divided into two seasons, an early season dominated by entry holes and a late season with mainly exit holes. The results showed a significant difference in emission rates from healthy and infested trees, independent of season. The seasonal average standardized BVOC emission rates of healthy trees was 32 ± 52 µg m^{-2} h^{-1} (mean ± standard deviation), while the average standardized BVOC emission rates of infested trees were 6700 µg m^{-2} h^{-1} and 2000 µg m^{-2} h^{-1} during early and late season respectively. BVOC emission rates decreased exponentially with time since infestation start and indicated induced emission rates for about one year after which the emission rates were similar to those from healthy bark. When comparing bark monoterpene BVOC emission rates with emission rates from needles, constitutive needle emission rates were found to be 11 times higher than the healthy bark emissions. However, the emission rates from infested Norway spruce tree bark were instead 6 to 20 times higher than the constitutive needle emissions, causing substantial increases in the total tree BVOC emission rate.

1 Introduction

In Europe, forest damage caused by outbreaks of the European spruce bark beetle (*Ips typographus*) is the third largest disturbance after storm-felling and forest fires (Jönsson et al., 2012; Schelhaas et al., 2003). In Sweden, the drought in the summer of 2018 led to increased bark beetle outbreaks which in 2020 were estimated to affect about 8 million m^3 (standing timber volume) Norway spruce (*Picea abies*) forest (Wulff and Roberge, 2020). This is the largest stock of forest volume killed by spruce bark beetles recorded in a single year in Sweden; in the period of 1990-2010, around 150,000 m^3 forest in southern Sweden was damaged on average per year (Wulff and Roberge, 2020). Climate change amplifies the risk of bark beetle outbreaks as the elevated risk of storm felling and drought favor the bark beetles with easier access to weakened trees (Jönsson et al., 2012). Higher temperatures and a longer growing season can also lead to an additional generation of spruce bark beetles per year (Jakoby et al., 2019; Jönsson et al., 2012). A larger bark beetle population, triggered by weather extremes, is associated with an increased risk of attacks on healthy spruce trees with outbreaks leading to extensive damage to the forests (Jakoby et al., 2019; Seidl et al., 2014).

Biogenic volatile organic compounds (BVOCs) emitted from trees function for example as a defense system against heat and oxidative stress (Loreto and Schnitzler, 2010). They are highly volatile and chemically reactive and can react directly with oxidizing species or act as membrane stabilizers (Brilli et al., 2009; Kleist et al., 2012; Sharkey et al., 2001). The efficiency of BVOCs to form oxidation products depends on the specific BVOC's molecular structure (Bonn and Moortgat, 2002; Roldin et al., 2019; Thomsen et al., 2021). As BVOCs are emitted, they can enhance chemical reactions which in turn can lead to increased tropospheric ozone concentration, or BVOCs can get oxidized and may foster the formation of secondary organic aerosol (SOA; Kulmala et al., 2003). Stress-induced BVOC emissions alter the oxidation capacity as some BVOC species are more efficient to act as SOA precursors and foster particle growth (Roldin et al., 2019; Thomsen et al., 2021). Boreal forests experiencing abiotic or biotic stress due to large-scale forest disturbances might thus increase the production of BVOC species highly efficient as precursors of SOA. This results in high uncertainties regarding the contribution to either a negative (cloud formation and radiation scattering (Paasonen et al., 2013)) or a positive feedback loop (increased tropospheric ozone) for the climate (Arneth et al., 2010; Jia et al., 2019).

Increased BVOC concentrations in plant tissue can also fight off predators (Laothawornkitkul et al., 2009; Li et al., 2019; Rieksta et al., 2020) and conifer trees use BVOCs as a defense mechanism against spruce bark beetles (Celedon and Bohlmann, 2019; Krokene, 2015; Raffa and Berryman, 1982). The parental bark beetles attack Norway spruce trees by drilling entry holes into the bark and form eggs galleries in the phloem. After about eight weeks, the new generation starts to leave the tree by drilling exit holes (Öhrn et al., 2014). To prevent a successful attack, the Norway spruce increase the resin flow which submerges the parental bark beetles and egg galleries, potentially killing beetles or pushing them out of the entry hole (Raffa, 1991). The resin serves as a storage pool containing BVOCs that volatilize when the resin is flowing out of the tree making the resin harden and close the wound. BVOCs are emitted constitutively from the trunk of the Norway spruce but when the emissions are induced as a stress-response they have been shown to be toxic to spruce bark beetles (Celedon and Bohlmann, 2019; Krokene, 2015), especially certain compounds like myrcene and α-terpinene (Everaerts et al., 1988). Studies on conifers attacked by bark beetles found evidence of increased monoterpene (MT) content at the attacked location (Amin et al., 2013; Ghimire et al., 2016; Zhao et al., 2011b). Occurrence of the oxygenated MT eucalyptol has been found to indicate induced defense and higher survival rates from Norway spruce attacked by spruce bark beetles (Schiebe et al., 2012). When comparing BVOC emission sources from different parts on conifer trees, trunk emissions are suggested to potentially contribute a lot more to the whole tree emissions than previously thought, even when not attacked by bark beetles (Greenberg et al., 2012).

There is still a lot to learn about the defense mechanism of Norway spruce, only a few studies have analyzed the induced BVOC emission from the trunk following an attack of the European spruce bark beetle (Ghimire et al., 2016; Zhao et al., 2011b). The aim of this study was to (i) investigate BVOC emissions from Norway spruce trunks and the impact of spruce bark beetles and to (ii) study the relation between BVOC emission rates, number of bark beetle drilled holes and time. The aim was also to (iii) compare and connect the spruce bark beetle induced BVOC emission rates to needle emissions and heat stress. Based on previous findings, three hypotheses were formulated: (H1) infested trees have higher bark emission rates than healthy trees and infestation change the emission blend, (H2) BVOC emission rates are highest at the start of infestation and decrease over time in response to declining tree vitality and eventual death of the tree and (H3) the type of the bark beetle drilled hole influence the BVOC emission rates where there is a relationship between the number of entry holes and emission rates rather than a high amount of holes. The reasoning behind H3 was that after a successful infestation, the number of holes increase after some weeks when the new generation leave the tree through exit holes, but the emission rates would decrease as the tree is dying due to bark damage and preventing transport of water and nutrients. In a sub-study, two trees with different initial health status were selected and followed throughout the growing season by repeating measurements during a successful attack and infestation of bark beetles. The aim (iv) of this sub-study was to see if the difference in initial health status of the trees would result in different emission rates and emission blends and to analyze how the individual emission blend changed over time after a successful infestation.

2 Methods

2.1 Site description

Six measurement campaigns were carried out from May to August 2019 (Table 1), where five campaigns were located at the ICOS (Integrated Carbon Observation System, ICOS-Sweden.se) research station in Hyltemossa (HTM, 56°06′N, 13°25′E; Fig. 1b) and one campaign at the ICOS research station in Norunda (NOR, 60°05′N, 17°29′E; Fig. 1b). The forest in HTM is dominated (>97% of the species composition) by Norway spruce (*Picea abies*) with a small fraction (<3%) of Scots pine (*Pinus sylvestris*) and deciduous trees. The understory vegetation is sparse, containing mostly mosses (Heliasz et al., n.d.). The forest in NOR is dominated by Norway spruce (54%) and Scots pine (37%) with a small fraction (9%) of deciduous trees and an understory vegetation with shrubs of mostly blueberries, cranberries, mosses and flowers (Mölder et al., n.d.). Both facilities are located inside managed forests, but the age and height of the trees differ. In HTM the trees are around 40 years old with an average height of 19 m in 2019 and NOR has a forest stand of mixed ages around 60-80 years and up to 110 years with a height of around 25 m for the dominating trees in 2019 (Heliasz et al., 2021; Mölder et al., 2021).

Table 1. Time table of the six campaigns conducted during 2019 at the sites Hyltemossa (HTM) and Norunda (NOR). Indicated is also the number of collected samples during each campaign at each plot and the status of the Norway spruce when measurements were collected (healthy or infested).

Month	**Date**	**Site**	**Number of collected samples**										
			Plot 1		Plot 2		Plot 3		Plot 4		Plot 5		Total
			Healthy	Infested	Healthy	Infested	Healthy	Infested	Healthy	Infested	Healthy	Infested	
May	4th-6th	HTM	12	3	12	-	12	-	-				39
June	4th-6th & 13th	HTM	9	1	12	-	6	6					34
July	2nd-4th	HTM	12	-	12	-	6	6					36
July-August	30th-1st	HTM	12	-	12	-	6	6					36
August	21st-22nd	NOR	-						-	9	-	9	18
August	26th-27th	HTM	12	-	12	-	-		-				24

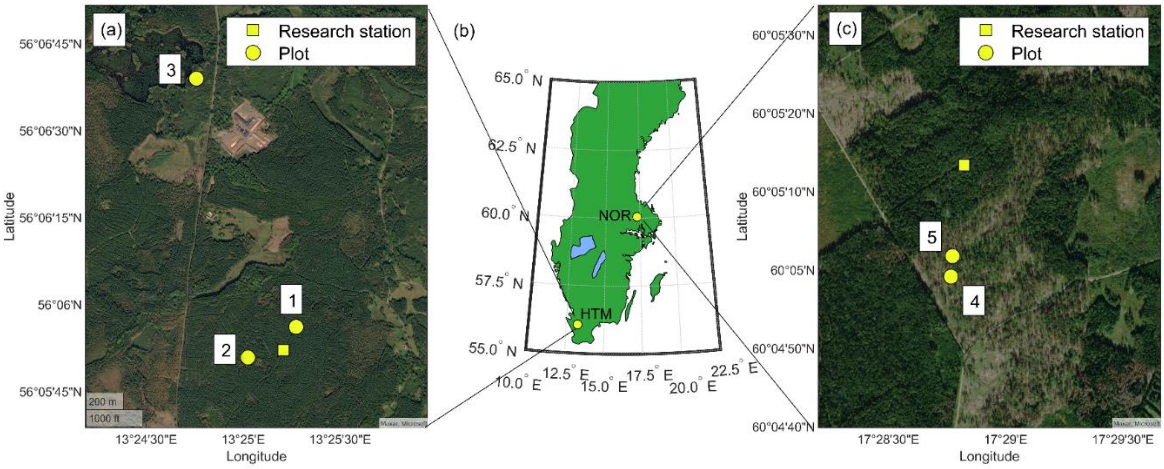

Figure 1: The location of the study sites with Hyltemossa (HTM; a) displayed to the left, the location in Sweden in the middle (b) and Norunda (NOR; c) displayed to the right. Measurement plots (yellow circle) at HTM (1-3) and NOR (4-5) are shown in the site-specific maps and their location relative to the ICOS station (yellow square). Healthy Norway spruce trees were measured in plot 1-3 and infested spruce trees were measured in plot 1, 3, 4 & 5. The sub-study was conducted in plot 3. The figure is created in MATLAB and Mapping Toolbox release 2021a (The MathWorks, Inc., Natick, MA, USA).

Three plots in HTM and two plots in NOR were selected for the study (Fig. 1a,c). Two plots in HTM were located inside the Norway spruce plantation used by ICOS, while the third plot was located around 1.6 km north of the ICOS station in an older (about 100 years) forest stand. In NOR the locations were chosen based on availability of bark beetle-affected trees inside the forest plantation. Four Norway spruce trees were selected at each plot in HTM, and three trees at each plot in NOR. A total of 18 trees were measured, whereof 12 were measured repeatedly during the growing season in HTM. Healthy trees were selected by visual examination in close contact with the forest manager employed by the forest owner, Gustafsborgs Säteri AB, in May 2019. Trees potentially stressed by forestry machinery or pests were not selected for the study. The infested trees were selected based on signs of spruce bark beetle infestation. Signs of late bark beetle infestation from the previous year, 2018, were found on two trees, one at plot 1 and one at plot 3. These trees were selected for the study to analyze long-term infestation effects. An active spruce bark beetle outbreak was occurring in NOR during 2019 and only infested trees were selected at that site.

The sub-study was conducted at plot 3 in HTM where two trees were selected, one already stressed from infestation in the previous year and one healthy (Fig. 1a). The healthy tree was baited using a bark beetle slit trap with pheromones to facilitate bark beetle infestation. The trap was installed between the campaigns in May and June (Table 1). One bag of biological attractant was used containing the pheromone 2,3,2 Methylbutenol (Typosan P306, Plantskydd AB, Ljungbyhed, Sweden). Both of the trees were successfully infested and measurements were repeated throughout the season to see the effects of infestation over time.

The weather during the measurement periods varied from cold and humid to warm and dry conditions. The average temperature during the growing season (May-August) was 14.6 °C (± 4.6 °C) in HTM and 14.2 °C (± 4.2 °C) in NOR with the sum of the precipitation over the growing season being 168 mm in HTM and 151 mm in NOR (Fig. 2). The daily average temperatures during the measurement periods ranged from 5 °C to 22 °C for both sites, with a daily total rainfall up to 3 mm (Fig. 2). In HTM, it was coldest (1 °C to 11 °C) during the measurement campaign in May and warmest (12 °C to 28 °C) during the measurement campaign in June.

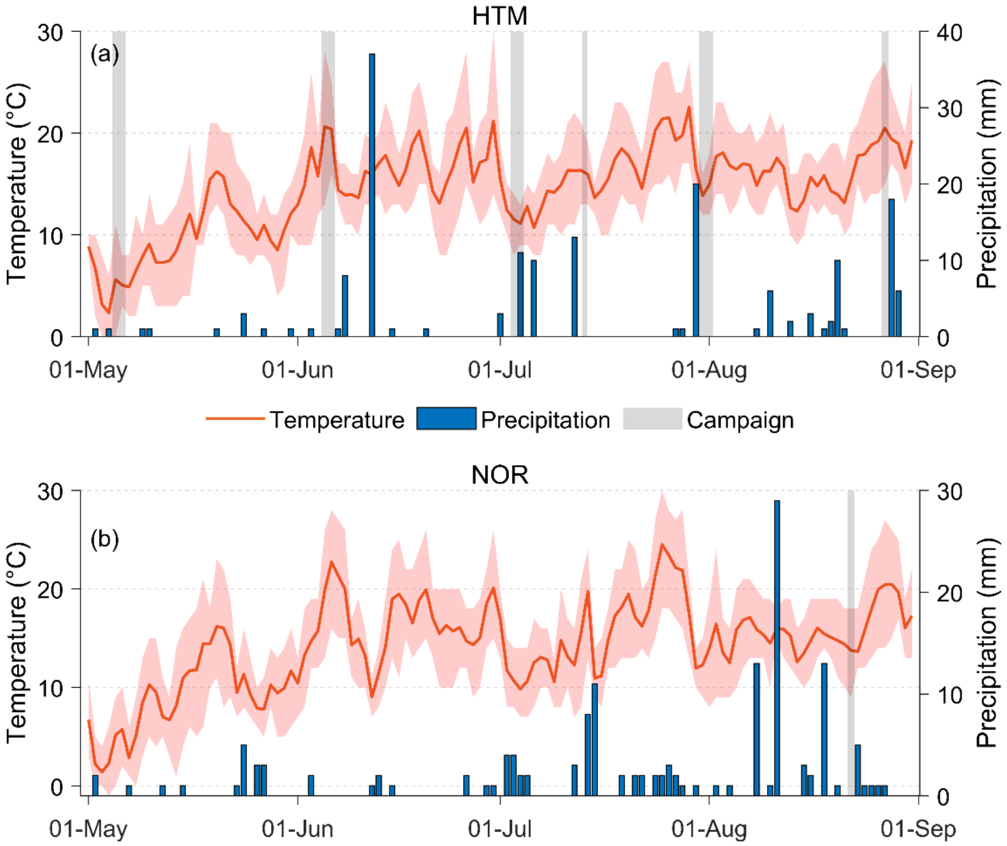

Figure 2: The daily average temperature (red line) with daily minimum and maximum temperature (red shade) and total daily precipitation (blue bars) for the study sites in (a) Hyltemossa and (b) Norunda. The times for the campaigns are marked in grey. The weather data was acquired from the ICOS research stations at the study sites (Heliasz, 2020; Mölder, 2021).

2.2 Experimental design

The bark emissions from the trees were measured using a tree trunk chamber connected with PTFE tubing (Teflon, Swagelok, Solon, OH, USA) to a pump box system consisting of a diaphragm pump (1420 VPD, Gardner Denver Thomas GmbH, Memmingen, Germany) and a flow meter (GFM mass flow meter, Aalborg Instruments & Controls Inc., USA). The pump box system was used to provide purge air with a flowrate of 0.7 lpm (liters per minute) to the trunk chamber with a volume of 0.6-0.9 L (Fig. 3). A BVOC filter (Hydrocarbon trap, Alltech, Associates Inc., USA) containing activated carbon and MnO_2-coated copper nets was mounted between the pump box and chamber to scrub the purge air of BVOCs and O_3. The chamber consisted of a metal frame and a flexible polyethylene foam base and was fastened with straps around the tree trunk. The inside of the chamber had been carefully wrapped with pre-conditioned (oven-cleaned 40 °C, 3 hours) polyamid bags (Toppits, Cofresco Frischhalteprodukte GmbH, Germany) to avoid contamination with BVOC from the chamber foam base. A metal lid with in- and outgoing PTFE-tubing (⌀ 6.35 mm) for purge air and sample collection was used to close the chamber during the measurement. Air temperature within the chamber was measured with a temperature probe (HI 145, Hanna Instruments, RI, USA) during BVOC collection and the bark surface temperature was measured with an infrared thermometer (IRT260, Biltema, Sweden) inside the chamber before and after each BVOC collection.

For each campaign, trees from one plot were sampled per day with BVOC collection starting around 08:00 (LT) and ending around 19:00 (LT) alternating sampling between the trees. The chamber bases were secured in place in the North or East orientation of the trunk every morning. The chambers were left open during the day to avoid built up concentrations of BVOCs inside the chambers. The bark temperature was measured at four different points inside the base prior to the sampling after which the lid was fastened and the chamber was flushed for 15 minutes before sampling started. Air temperature inside the chamber was measured at the start and at the end of the BVOC collection to note potential temperature differences during the sample period. After sampling, the lid was removed and the bark temperature was measured again.

The start of the infestation was determined by the beetles' swarming time in relation to when the tree infestation was detected. For plot 3 in HTM the start of the infestation was seen during the campaign in June (Table 1). For the other plots the swarming time was retrieved using data from Skogsstyrelsen Statistical Database (Skogsstyrelsen, n.d.) taken at the plots closest to the measurement sites (Supplementary material, Table S1, Table S2). A late swarm in HTM was detected around week 25-28 for 2018 (Fig. S1), and a main swarm in NOR around week 20-21 for 2019 (Fig. S2)

The bark inside the chamber was controlled visually before each measurement to count the number of bark beetle holes and to assess potential lichen and algal cover. By looking at bark photos, the holes were later separated into entry or exit holes for the infested trees (Fig. 4). The separation depended on the characteristics of the hole where entry holes were determined to have more resin bleed compared to exit holes, which also had a rounder shape. The number of holes counted inside the chamber area is listed in Table 2 along with an extrapolation of the counted holes from the chamber area to square meter bark area. Entry holes were found for measurements taken up to 100 days after infestation and exit holes were predominantly found for measurements taken after 100 days of infestation, with the latest measurement occurring 350 days after estimated infestation start. As the two hole types were consistently occurring before or after 100 days since infestation start, the measurements with mainly entry holes is referred to as the early season and the measurements with mainly exit holes as the late season.

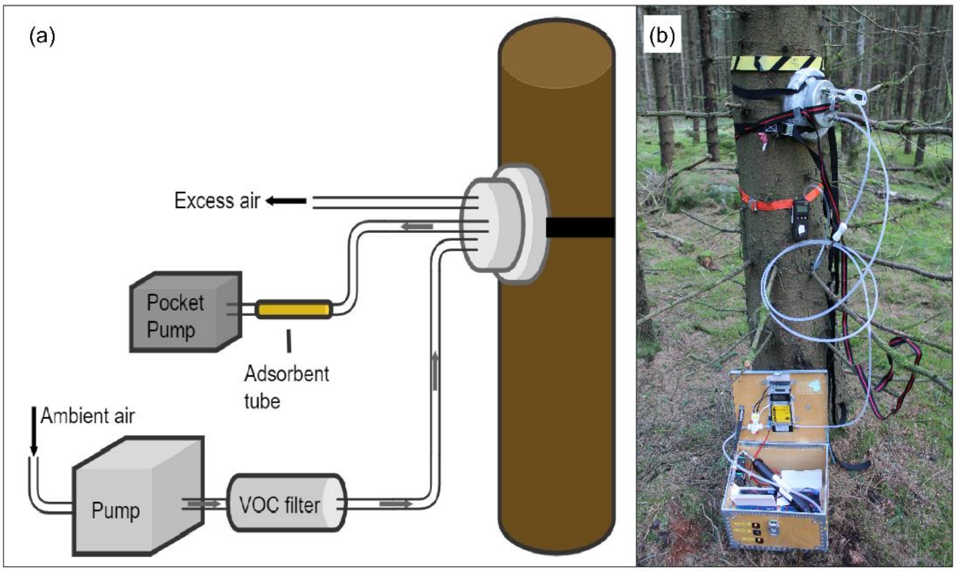

Figure 3: The experimental setup (a) and a field photo (b) of the tree trunk chamber mounted on a Norway spruce trunk. The chamber is connected to a pump box used to provide BVOC- and O_3-free purge air. The BVOC samples were collected with adsorbent tubes by extracting the air from the chamber using a pocket pump.

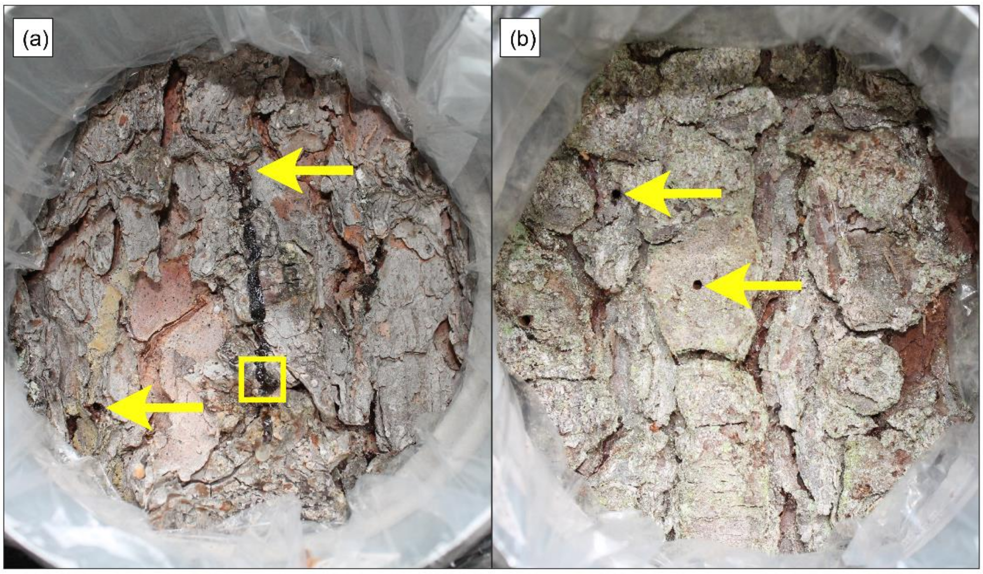

Figure 4: Examples of infested Norway spruce trees with (a) entry and (b) exit holes. The arrows indicate examples of bark beetle drilled holes and the square box frames a bark beetle. There are more holes in the pictures than indicated by the arrows.

Table 2. The infested Norway spruce trees by tree ID, site, plot and the number of holes counted inside the chamber at the given date for each tree. The counted holes were upscaled to holes per square meter of bark surface and the majority of the hole type was determined to either mostly entry or exit holes. The Norway spruce with the ID S1S1 was infested during the late season 2018 and had thus already a majority of exit holes early in 2019.

Tree ID	Site	Plot	Date	Number of holes inside chamber	Upscaled to holes per m^2	Hole type majority
S1S1	HTM	1	2019-05-04	12	1062	exit
S1S1	HTM	1	2019-06-05	8	708	exit
S3S2	HTM	3	2019-06-04	4	354	entry
S3S3	HTM	3	2019-06-04	5	442	entry
S3S2	HTM	3	2019-07-03	3	286	entry
S3S3	HTM	3	2019-07-03	5	465	entry
S3S2	HTM	3	2019-08-01	6	531	entry
S3S3	HTM	3	2019-08-01	15	1273	entry
S4S1	NOR	4	2019-08-21	4	354	exit
S4S2	NOR	4	2019-08-21	5	442	exit
S4S3	NOR	4	2019-08-21	5	442	exit
S5S1	NOR	5	2019-08-22	5	442	exit
S5S2	NOR	5	2019-08-22	4	340	exit
S5S3	NOR	5	2019-08-22	7	619	exit

2.3 BVOC sampling and analysis

A total of 187 samples were taken, where 147 samples were from healthy Norway spruce and 40 were from infested Norway spruce (Table 1). Stainless steel cartridges (Markes International Limited, Llantrisant, UK) packed with adsorbents Tenax TA (a porous organic polymer) and Carbograph 1TD (graphitized carbon black) were used to sample BVOCs. The BVOCs were sampled from the chambers using flow-controlled pocket pumps (Pocket Pump, SKC Ltd., Dorset, UK) by extracting the air through the steel cartridges at a flow rate of 200 ml min^{-1} and a sampling time of ca. 30 minutes. The collected volume for each sample was between 5 to 6 L. Blank samples were collected from the chamber inlet air twice per day, once before the first sample and once after the last sample to capture possible background contamination. The method was repeated throughout the day until all trees of that plot were measured three times.

After collecting the BVOC samples, the adsorbent cartridges were capped and stored in a refrigerator (at ~3 °C) before being analyzed using a two-stage automated thermal desorption apparatus coupled to a gas-chromatograph mass-spectrometer. Desorption was done on a Turbomatrix ATD 650 (PerkinElmer, Waltham, MA, USA) by primary heating the cartridges to 280 °C in a flow of purified helium (He, ALPHAGAZ 1, Air Liquide Gas AB, Sweden) for 10 minutes, in order for the BVOCs to volatilize. After the primary desorption, BVOCs were cryo-focused downstream on a Tenax TA cold trap maintained at –30 °C. The cold trap was flash-heated (40 °C sec^{-1}) to 300 °C for 6 minutes to perform a second desorption. The volatilized BVOCs were passed via a heated transfer line using He as carrier gas, to a gas chromatograph-mass spectrometry system (GC-MS, Shimadzu QP2010 Plus, Shimadzu Corporation, Japan). The BVOCs were separated using a BPX5 capillary column (50 m, I.D. 0.32 mm, film thickness 1.0 µm, Trajan Scientific, Australia) and the oven temperature was initially held at 40 °C for 1 minute, raised to 210 °C at a rate of 5 °C min^{-1} and further increased to 250 °C at a rate of 20 °C min^{-1} and lastly held for 2 minutes. Pure standard solutions of isoprene, α-pinene, β-pinene, p-cymene, eucalyptol, limonene, 3-carene, linalool, α-humulene, β-caryophyllene, longifolene and myrcene were pre-prepared in methanol (Merck KGaA, Darmstadt, Germany) and injected onto adsorbent cartridges in a stream of He and analyzed as samples. When quantifying BVOCs for which no standards were available, α-pinene was used for MTs, and α-humulene for sesquiterpenes (SQT). For other BVOCs which did not match any standard, the amount of the compound present on the sample was calculated as a percentage of the total amount on the sample using the chromatogram peak area. The peaks of longifolene and β-caryophyllene where coeluted in the chromatography and are therefore presented together as a sum of two compounds in this study. The chromatogram peaks were identified based on comparison with retention times and mass spectra of standards and the mass spectra in the NIST08 library. LabSolutions GCMS post run analysis program was used for data processing (Version 4.30, Shimadzu Corporation, Japan). Detection limit was set to 0.4 ng in the analysis software based on the analysis of blank samples.

Two outliers in the BVOC samples were found from two Norway spruce trees located at plot 1 in HTM (Fig. 1a). The bark was examined with bark photos and it was detected that the chamber in both cases had been placed upon a small emerging branch with some spots of resin as well as with one single needle stuck on the bark. This was believed to have caused the outliers and these samples were considered unusable and excluded from further analysis. All samples from one Norway spruce at plot 2 were also excluded from the analysis after discovering placements on top of a bark hole likely not originating from spruce bark beetles, and thus not suitable in this study.

2.4 Emission rate calculation and standardization

The BVOC concentrations obtained from the sample analysis were converted to emission rate (ER) (µg m^{-2} h^{-1}) according to Eq. (1), following Ortega & Helmig (2008):

$$ER = \frac{[C_{out} - C_{in}]Q}{A}, \tag{1}$$

where C_{out} (µg l^{-1}) is the concentration of each compound within the chamber, and C_{in} (µg l^{-1}) is the concentration of the compound in the filtered inlet air, Q is the flow rate through the chamber (l min^{-1}) and A is the bark surface area (m^{-2}) inside the chamber.

The ER per hole was calculated as the average by dividing the ER derived from Eq. (1) for the respective sample with the number of counted holes (Table 2) according to Eq. (2):

$$ER\ per\ hole = \frac{ER}{\#\ \mathrm{holes}}, \tag{2}$$

Finally, the ER for one square meter of bark surface, ER_{sqm}, was extrapolated based on the number of holes within the chamber and the chamber's bark area according to Eq. (3):

$$ER_{sqm} = \mathrm{ER} \cdot \#\mathrm{holes} \cdot \frac{1}{A}, \tag{3}$$

The emission rates of the infested Norway spruce trees were scaled with an average of the holes per square meter found for the measured trees in HTM and NOR (Table 2). By doing this, any variation in emission rate caused by a difference in amount of holes was removed which enabled more accurate comparison between the infested trees.

As the bark surface temperature varied over the season and between the days, the emission rates were standardized using the algorithm for stored, temperature dependent BVOCs by Guenther et al., (1993; G93) according to Eq. (4):

$$M = M_S \cdot e^{(\beta(T-T_S))}, \tag{4}$$

where M is the emission rate (µg m^{-2} h^{-1}) at a given bark temperature, T, and β (0.09 K^{-1}) is an empirical coefficient establishing the temperature dependency (Guenther et al., 1993). M_s is the emission rate at standard temperature T_s of 30 °C.

The temperature sensitivity of compound emission rates was calculated using a Q_{10} relationship (Lloyd and Taylor, 1994) following Seco et al. (2020) where the Q_{10} coefficient represents the factor by which the compound emission rate increases for every 10 °C temperature increase from a reference emission rate, F_0. Only compounds appearing in more than three individual samples were selected for further analysis using this method. Log transformed emission rates were binned into 1 °C bins and the mean emission rate per bin was calculated except for bins with only one value. An orthogonal distance regression was applied to the binned mean emission rates weighed by their standard deviation to determine Q_{10} and F_0 using Eq. (5):

$$F = F_0 \cdot Q_{10}^{(T-T_0)/10}, \tag{5}$$

where F_0 is the reference emission rate at temperature T_0 (30 °C), F is the flux rate at bark surface temperature T (°C), and Q_{10} is the temperature coefficient.

Based on the Guenther algorithm (G93, Guenther et al., 1993; Eq. (4)) and the Q_{10} temperature dependency calculation (Q_{10}, Lloyd and Taylor, 1994; Eq. (5)) an estimation of the total BVOC emission rate from healthy Norway spruce bark and the needle BVOC emission rate throughout the season was calculated. Both algorithms were used to calculate bark BVOC emissions, while only G93 was used to calculate the needle emission, as well as bark SQT emission rate. The calculated emissions for bark was based on the measured tree trunk temperature from the ICOS ecosystem data in HTM (Heliasz, 2020), taken at 3 m height. An average of the trunk temperature measurements taken in the North and East orientation of the trunk was used for this.

The needle emissions for MT and SQT were calculated according to Eq. (4) using the standardized seasonal average emission rate (M_s), 1.25 µg g(dw)$^{-1}$ h^{-1} for MT and 0.34 for SQT µg g(dw)$^{-1}$ h^{-1}, taken from van Meeningen et al. (2017) measured in HTM during 2016. The temperature input was the canopy-level air temperature measured at 24 meter agl. taken from the HTM ICOS station (Heliasz, 2020). The output of Eq. (4) was scaled from g(dw) to m^2 by using a specific leaf area (SLA) of 38.4 cm^{-2} g^{-1} calculated from Wang et al. (2017).

2.5 Statistical analysis

All samples were tested for normality by creating normal probability curves (normplot, MATLAB R2021a, The MathWorks, Inc., MA, USA) which indicated no normal distribution in the data. Statistical analysis of all measurements were thus performed using a Kruskall-Wallis test (MATLAB R2021a, The MathWorks, Inc., MA, USA) with a level of significance set to $P<0.05$. To assure that no deviation between the plots of the healthy Norway spruce trees in HTM occurred, the following scenario was tested: 1) the difference in emission rates from the healthy trees at plot 1, 2 and 3 in HTM. To test the study aim and hypotheses, the following scenarios were tested: 2) the difference in emission rates from healthy and infested trees from all plots and sites (H1), 3) the difference in emission rates from one initially healthy spruce and one initially stressed spruce (aim (iv)) and 4) the difference between the calculated Q_{10} coefficient and F_0 for the healthy and infested trees (aim (iii)).

To test H2 and H3, an exponential function (Curve Fitting Toolbox, MATLAB R2021a, The MathWorks, Inc., MA, USA) was fitted to the data using (Eq. 6):

$$f(x) = a \cdot e^{b \cdot x}, \tag{6}$$

where x is the emission rate in µg m^{-2} h^{-1}. The following scenarios were compared: 1) emission rates from infested Norway spruce and the evolvement over time (H2) and 2) emission rates from infested Norway spruce and the number and type of bark beetle holes (H3).

3 Results

3.1 Bark BVOC emissions from healthy and infested Norway spruce

For the healthy Norway spruce trees in HTM, the average total temperature standardized bark BVOC emission rate from all samples (n=113) was 32 ± 52 µg m^{-2} h^{-1} (mean ± standard deviation; Table 3). The most dominant BVOC group was MTs (29 ± 51 µg m^{-2} h^{-1}; Table 3) followed by SQTs (2.1 ± 3.2 µg m^{-2} h^{-1}; Table 3). Isoprene emissions were detected in 58% of total samples from the healthy spruce bark with an average emission rate of 0.4 ± 0.9 µg m^{-2} h^{-1} (Table 3).

The variability of the emission rates differed little between the plots in HTM. The standardized emission rates were ranging from 0-145 µg m^{-2} h^{-1}, for plot 1, 0-94 µg m^{-2} h^{-1} for plot 2 and 1-235 µg m^{-2} h^{-1} for plot 3 where the median emission rate were 4, 17 and 8 µg m^{-2} h^{-1} respectively (Fig. 5). No statistically significant difference ($P>0.3$) was found for the emission rates between the plots and no clear pattern of diurnal variation was found in the samples.

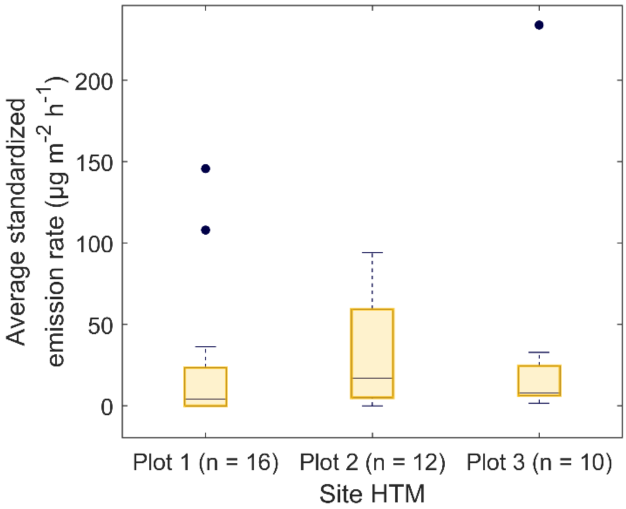

Figure 5: Boxplots of the temperature standardized emission rates of the healthy trees for plot 1-3 in Hyltemossa, where plot 3 is located furthest away from the station in an older forest stand. The number of samples taken at each plot is indicated by n, the black dots indicate outliers. The difference in emission rates was tested using a Kruskall-Wallis test (MATLAB R2021a, The MathWorks, Inc., MA, USA) and indicated no significant difference for the daily average of the total temperature standardized emission rates (*P*>0.3).

For the bark beetle infested trees located in both sites (HTM and NOR), the average total temperature standardized emission rate for Norway spruce infested in the early season (n = 6) was 6,700 ± 6,900 µg m^{-2} h^{-1} (mean ± standard deviation; Table 3). The average for trees infested in the late season (n = 8) was 2,000 ± 1,300 µg m^{-2} h^{-1} (Table 3). MTs was the most dominant BVOC group throughout the season with an average of 6,600 ± 6,700 µg m^{-2} h^{-1} for the early season and 1,900 ± 1,300 µg m^{-2} h^{-1} for the late season, followed by SQTs (early: 53 ± 74 µg m^{-2} h^{-1}, late: 18 ± 24 µg m^{-2} h^{-1}; Table 3). Throughout the season, isoprene was also found in 42 % of the samples with an average emission rate of 3.4 ± 6.7 µg m^{-2} h^{-1} during the early season and 0.1 ± 0.2 µg m^{-2} h^{-1} for the late season (Table 3).

For all measured Norway spruce trees at both sites, a total of 74 individual BVOCs were found throughout the measurement period for all samples (n = 151) whereof 32 were MTs, 5 were SQTs and 37 were classified as other BVOCs including isoprene. For the healthy Norway spruce tree samples in HTM (n = 113), 44 individual compounds were found in total, where 12 were MTs, 2 were SQTs and 30 other BVOCs including isoprene. The infested Norway spruce trees measured at both sites had less samples (n = 38) compared to the healthy tree but a higher number of individual compounds was found with 52 compounds in total where the majority of the compounds were MTs (n = 30) which was more than the double compared to the healthy trees. There were also more SQTs (n = 5) found in the infested tree samples, but less other BVOCs including isoprene (n = 17) compared to the healthy tree samples. For the infested trees, there was also a difference in how many compounds were found early in the season compared to later, in total 40 individual compounds were found for the early and 33 compounds for the late season (Table 3). For MTs and SQTs, more individual compounds were found in the early season (27 MTs & 5 SQTs) compared to the late season (17 MTs & 2 SQTs), but for the other BVOCs more were found in the later season which had 14 individual compounds identified compared to 8 in the early season.

A significant difference was found for the daily average of the total standardized bark BVOC emission rate when comparing healthy and infested trees from all plots and sites, for both early and late season (*P*<.001; Fig. 6). During the early season, the infested trees had a median emission rate of 6,400 µg m^{-2} h^{-1} and 2,100 µg m^{-2} h^{-1}

during the late season (Fig. 6). The emission rates for infested trees during the early and late season were around 740- and 240-fold higher compared to the median of the healthy trees (8.6 µg m^{-2} h^{-1}; Fig. 6).

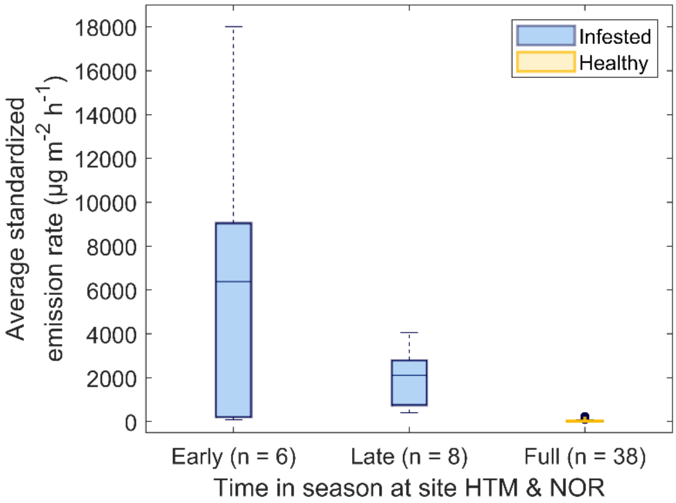

Figure 6: Boxplots of the temperature standardized emission rates of the infested Norway spruce trees (blue) during the early and late season and the healthy Norway spruce trees (yellow) during the full season. The healthy trees were measured in Hyltemossa and infested trees were measured both in Hyltemossa and Norunda. To consider the seasonal pattern of the spruce bark beetle, the infested trees were divided into early and late season, where the early season is dominated by entry holes and the late season by exit holes. The number of samples taken at each plot is indicated by n and the black dots indicates outliers. The difference in emission rates for the infested and healthy trees was tested using a Kruskall-Wallis test (MATLAB R2021a, The MathWorks, Inc., MA, USA) which indicates significantly higher emission rates from infested trees during both seasons compared to the healthy trees (*P*<.001 for both).

A difference between the healthy and infested trees from both sites was also apparent in the occurrence of the compounds throughout the samples (Table 3). The most common MT compounds among the healthy Norway spruce trees were α-pinene (76 %, relative occurrence in all samples), β-pinene (55 %), 3-carene (48 %) and limonene (44 %). For infested Norway spruce trees in both seasons, the mentioned MTs were also the most occurring compounds but they also occurred in more samples (88-100 %). The late season also had 100 % occurrence of (1S)-camphene while that compound only occurred in 75 % of the samples for the early season. For SQTs, α-humulene occurred most among the healthy trees (47 %) followed by longifolene+β-caryophyllene (17 %). For the infested trees in the early season the pattern was reversed, the SQTs occurring most were longifolene+β-caryophyllene (56 %) followed by α-humulene (31 %). The late season showed a similar pattern where longifolene+β-caryophyllene occurred most (55 %) followed by α-humulene (18 %) which occurred in fewer samples compared to the early season. The SQTs germacrene D, isoledene and β-cubebene were found to be emitted from one infested tree during the early season, but was not discovered any other time. Isoprene was found to be mostly occurring among the other BVOCs for both the healthy (58 %) and infested Norway spruce during the early and late season (63 % and 27 % respectively). After isoprene, decanal (45 %), benzene (45 %), nonanal (38 %) and toluene (21 %) were occurring most for the healthy Norway spruce. For the early season infested Norway spruce trees, 2-methyl-1-phenylpropene (38 %) and 2-methyl-3-buten-2-ol (19 %) were occurring most after isoprene, however, this was not the case for the infested trees in the late season where 2-methyl-3-buten-2-ol was not emitted and 2-methyl-1-phenylpropene occurred in 9 % of the samples.

Comparing the emission rates from infested trees to healthy trees, the emission rates showed increases for all individual compounds ranging from a 3-fold increase to a 2580-fold increase for both early and late season (Table 3). The group of MTs had the highest (230-fold) increase during the early season compared to SQTs (25-fold increase) and isoprene (8-fold increase). The emission rates during the late season showed a 65-fold increase for the MTs and 8-fold for the SQTs, however, isoprene was found to have a 0.4-fold decrease from the infested tree emission rates in the late season compared to healthy tree emission rates. The compound (+)-sabinene had the highest increase of all individual compounds (2580-fold) during the early season when comparing healthy and infested tree emission rates (Table A1). The compounds: tricyclene, eucalyptol, 4-carene, ζ-fenchene, α-phellandrene, (4E,6E)-alloocimene, norbornane, γ-terpinene, α-fenchene, 2-carene, α-thujene, α-terpinene were only emitted from infested trees and indicate a change in the chemical composition of the emitted BVOCs (full table is found in Appendix Table A1).

Table 3. Seasonal average temperature standardized emission rate (µg m^{-2} h^{-1} ± one standard deviation) from all Norway spruce trees located in Hyltemossa and Norunda. Presented are the frequently occurring unique compounds, compound groups (Monoterpenes, sesquiterpenes and other BVOCs) and total BVOCs emitted from healthy and infested (early and late season) Norway spruce bark. The increase or decrease (%) is presented for the infested trees as a change in emission rate from healthy to infested. The occurrence (%) indicates how often each compound appeared in the samples throughout the growing season. The compounds that were identified but unable to quantify are presented as n.q. (no quantification). A full list of all identified compounds is found in the Appendix (Table A1).

	Healthy		**Infested early season**			**Infested late season**		
Compound name	*average ± std (µg m^{-2} h^{-1})*	*occurrence (%)*	*average ± std (µg m^{-2} h^{-1})*	*increase (%)*	*occurrence (%)*	*average ± std (µg m^{-2} h^{-1})*	*increase (%)*	*occurrence (%)*
Monoterpenes	29 ± 51		6,600 ± 6,700	22,400		1,900 ± 1,300	6,500	
α-Pinene	12 ± 20	76	910 ± 1030	7,800	100	820 ± 890	7,100	100
β-Pinene	8 ± 19	56	950 ± 960	11,500	100	230 ± 170	2,600	100
3-Carene	3 ± 5	49	290 ± 420	11,400	100	30 ± 40	1,200	95
Limonene	2 ± 3	44	320 ± 320	16,900	88	90 ± 80	4,400	100
p-Cymene	1 ± 1	40	240 ± 320	49,200	63	50 ± 40	10,700	77
β-Myrcene	0.3 ± 0.8	18	160 ± 170	49,800	79	10 ± 6	1,900	86
β-Phellandrene	3 ± 8	11	670 ± 660	24,800	44	190 ± 160	6,900	68
(1S)-Camphene	2 ± 6	6	1,520 ± 1,970	89,100	75	390 ± 230	22,800	100
(+)-Sabinene	0.1 ± 0	1	210 ± 200	257,900	44	3 ± 0	3,600	5
Sesquiterpenes	2.1 ± 3.2		53 ± 74	2,400		18 ± 24	700	
Longifolene+β-Caryophyllene	0.7 ± 1.4	18	38 ± 70	5,300	56	14 ± 24	1,800	55
α-Humulene	1.4 ± 3	48	5 ± 9	200	31	4 ± 13	200	18
Germacrene D	-	-	4	-	19	-	-	-
Isoledene	-	-	3	-	19	-	-	-
β-Cubebene	-	-	3	-	19	-	-	-
Other BVOCs	0.4 ± 0.9		3.4 ± 6.7			0.1 ± 0.2		
Isoprene	0.4 ± 0.9	58	3 ± 7	700	63	0.1 ± 0.2	-65	27
Decanal	n.q	45	n.q	-	13	n.q	-	14
Benzene	n.q	45	-	-	-	n.q	-	14
Nonanal	n.q	39	n.q	-	6	n.q	-	14
Toluene	n.q	21	n.q	-	6	n.q	-	9
2-Methyl-1-phenylpropene	-	-	n.q	-	38	n.q	-	9
2-Methyl-3-buten-2-ol	-	-	n.q	-	19	-	-	-
Total	32 ± 52		6,700 ± 6,900	20,900		2,000 ± 1,300	6,000	

3.1.1 Scaling the infested tree bark emission with number of bark beetle holes

The temperature standardized emission rates (TS) for the total BVOCs from the bark beetle infested Norway spruce trees from both sites were ranging from around 500 to 13,000 µg m^{-2} h^{-1} throughout the measurement period (Fig. 7). The daily average TS emission rate per bark beetle hole for infested trees during the early season was 22 ± 29 µg $hole^{-1}$ h^{-1} and 4.4 ± 3.5 µg $hole^{-1}$ h^{-1} for the late season. When scaling the TS emission rates with the average number of bark beetle holes (BBH), a comparison with only the TS emission rates showed that the total average of BBH emission rates were higher (Fig. 7). During the early season the BBH emission rates were about 2,500 µg m^{-2} h^{-1} higher (9,200 ± 6,200 µg m^{-2} h^{-1}) compared to TS emission rates (6,700 ± 5,000 µg m^{-2} h^{-1}) and for the late season the BBH emission rates were 150 µg m^{-2} h^{-1} higher (900 ± 650 µg m^{-2} h^{-1}) compared to TS emission rates (750 ± 400 µg m^{-2} h^{-1}). For the individual trees the BBH emission rates of MT increased compared to TS emission rates for all trees but two (tree S1S1 and tree S5S3) where the TS emission rates were about 300 µg m^{-2} h^{-1} higher (Fig. 7). The inconsistent variation in emission rates scaled with BBH or TS can be explained by the difference in number of bark beetle holes found per tree (Table 2). The TS emission rates only consider the bark beetle holes inside the bark chamber while the BBH emission rates are calculated based on holes extrapolated to average holes per square meter. By applying an average of the bark beetle holes found in this study to all trees, variations in emission rates caused by a different amount of holes can be disregarded. The results from the infested trees are thus from here on presented as BBH emission unless stated otherwise.

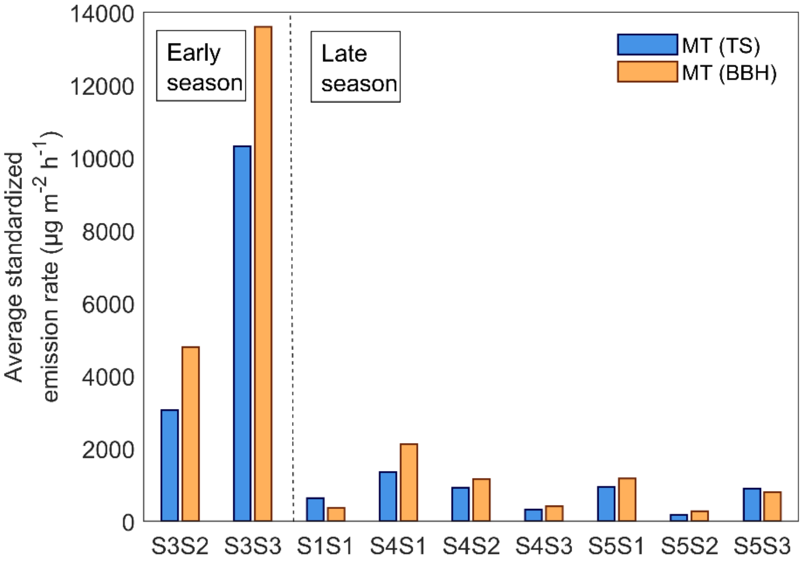

Figure 7: The seasonal average temperature standardized emission rate for the group of monoterpenes (MT) from all infested Norway spruce trees located in Hyltemossa and Norunda. The tree ID is presented at the x-axis and is separated into early and late season (less or more than 100 days since infestation start). The temperature standardized emission rates (TS) are presented in blue, while the emission rates also scaled by the average number of bark beetle holes (BBH) is presented in orange.

3.2 The influence of time since infestation on emission rate from infested trees

To study the influence of time on the emission rates after Norway spruce trees were infested by spruce bark beetles, measurements were taken at different occasions in relation to infestation start in both HTM and NOR. The earliest measurements occurred 12 days after infestation and showed an average emission rate for the total BVOCs of around 1,900 µg m^{-2} h^{-1}, when excluding a tree with lowered defence (as presented in Sect. 3.4; Fig. 8a; excluded tree is marked in yellow). An exponential function was fitted to all data points according to Eq. 6. Three compounds were selected for further analysis, β-phellandrene, eucalyptol and β-pinene, using the same exponential function. The emission rates after 12 days were different for the individual compounds compared to the total average, β-phellandrene and β-pinene have emission rates of around 3,000-3,500 µg m^{-2} h^{-1} and 2,000-2,500 µg m^{-2} h^{-1} respectively (Fig. 8b,d). Eucalyptol was emitted at lower rates of around 4 and 25 µg m^{-2} h^{-1}, where the low emission rates came from the lowered defence tree (Fig. 8c). Some compounds were not emitted from all infested trees: eucalyptol was only observed from 4 individual trees, and β-phellandrene from 7 trees, while β-pinene was emitted from all infested trees (n = 9).

After about 100 days since start of infestation, the trees were showing signs of browning and loss of needles and emission rates for the total BVOCs showed a 5-fold decrease on average, emitting around 300 µg m^{-2} h^{-1}. The emission rates were still at levels higher than the seasonal emissions from healthy Norway spruce trees in HTM (around 30 µg m^{-2} h^{-1}; Fig. 8). Compared to the emission rate of the total BVOCs after 100 days since infestation, the emission rates from the compounds β-phellandrene and β-pinene were at about the same level, however, the decrease on average since the start of infestation was higher (around 9-fold). Eucalyptol did not have an as distinct decrease but had only decreased with 1-fold on average. When the Norway spruce with ID S1S1 located in plot 1 in HTM was measured after more than 300 days since infestation start it had lost almost all of its needles and some bark. At that time, the total BVOC emission rates from that tree were around 40 µg m^{-2} h^{-1}, which was at the same level as the emissions from healthy trees at the same time (on average 38 µg m^{-2} h^{-1}; Fig. 8). No emissions of eucalyptol were found after more than 300 days, but the emission rates of β-phellandrene and β-pinene after 315 days post infestation were around 70 and 270 µg m^{-2} h^{-1} respectively, however, after 350 days the emission rates went down to around 32 and 58 µg m^{-2} h^{-1} respectively, also comparable with the emissions from healthy trees at that time (around 45 µg m^{-2} h^{-1}).

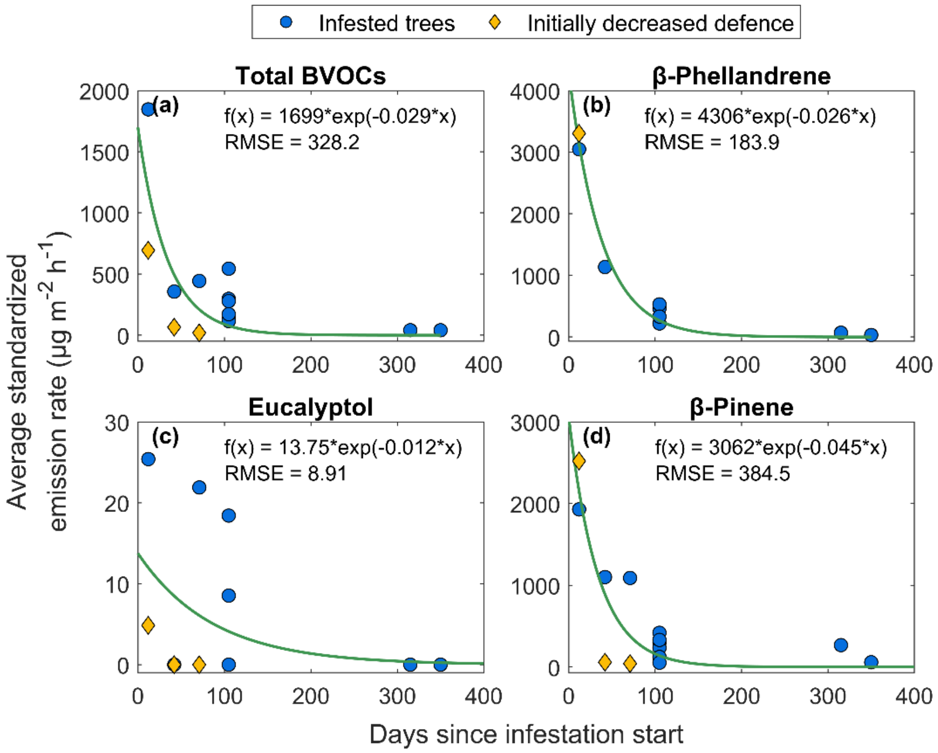

Figure 8: The relationship between average temperature standardized emission rate from all infested Norway spruce trees (blue circle) in Hyltemossa and Norunda and the number of days since infestation start for (a) total BVOCs, (b) β-phellandrene, (c) eucalyptol and (d) β-pinene. An exponential curve was fitted to the data according to Eq. 6 (green line). All trees are included in the exponential fitted curve, however one tree had initially lowered defence and marked specifically in the figure (yellow diamond).

3.3 The difference in BVOC emission rates from bark beetle entry and exit holes

No clear relationship was found between the total number of holes and emission rates, likely due to a mixed signal from the type (entry or exit) and time since infestation. The total BVOC temperature standardized emission rates were generally lower from exit holes compared to entry holes when the Norway spruce trees had similar amounts of holes (Fig. 9a). The individual compounds emitted from both entry and exit holes were dominated by β-phellandrene, β-pinene, α-pinene and (1S)-camphene (Table 3). The compounds found from entry holes but not from exit holes were: 2-carene, 4-carene, α-fenchene, α-phellandrene, α-terpinene, α-thujene, β-cubebene, ϒ-terpinene, germacrene D, isoledene and (4E,6E)-alloocimene (Table 3). Generally lower emission rates from exit holes were also seen for the compounds β-phellandrene and β-pinene (Fig. 9b,d). However, for the compound eucalyptol (Fig. 9c) emissions were only found from four individuals, which had similar emission rates regardless of entry or exit holes. The oxygenated monoterpenes myrtenal and bornyl acetate were only found in entry holes but could not be quantified (Table 3).

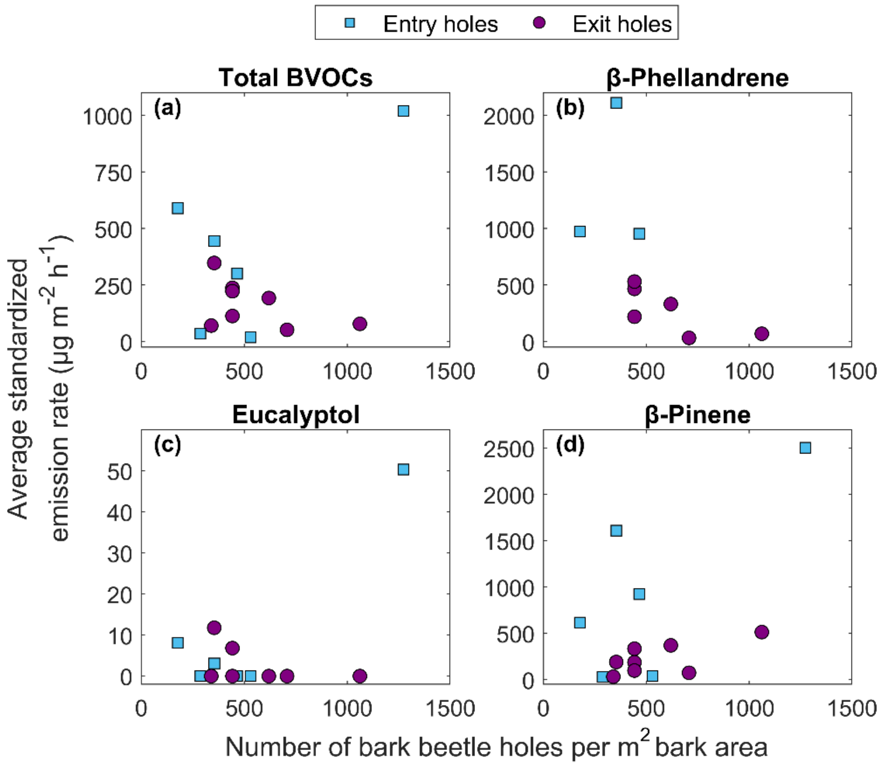

Figure 9: The relationship between average temperature standardized emission rate from infested Norway spruce trees in Hyltemossa and Norunda and the number of bark beetle holes per m^2 bark area for (a) total BVOCs, (b) β-phellandrene, (c) eucalyptol and (d) β-pinene. The bark beetle holes are separated into entry holes (blue squares) and the exit holes (purple circles).

3.4 Bark beetle infestation impact over time from two trees with different initial health status

As a part of the sub-study, a bark beetle trap was installed at plot 3 in HTM (Fig. 1). This resulted in successful bark beetle infestation of two Norway spruce trees with different initial health status, one healthy (tree ID S3S3) and one stressed (tree ID S3S2). The different status of the trees can be identified in Fig. 10 (a,b) where S3S2 had significantly higher (P>0.02) total emission rate of bark BVOCs in May, before the infestation, compared to the healthy Norway spruce (S3S3). The remaining two Norway spruce trees on plot 3 were not infested and an average of the emission rates from these trees were taken to compare with the infested trees. Only four compounds for the healthy trees were found in May, longifolene+β-caryophyllene, α-humulene and isoprene (Fig. 10a,b) and the healthy trees remained at low emission rates for the remaining months (Fig. 10). The total emission rates for S3S3 and S3S2 were induced in June when the bark beetle infestation started (Fig. 10c,d). There was no significant difference (*P*>0.2) in emission rates between the trees, but the compound blend differed between the S3S3 and S3S2. The tree S3S3 had a higher emission rate from the compound (1S)-Camphene and was also emitting ζ-fenchene, (4E,6E)-alloocimene, norbornane and α-thujene which were not emitted from S3S2. The samples from S3S2 in June (Fig.10c,d) did however contain the bark beetle pheromones germacrene D, isoledene and β-cubebene which were not found in the compound blend from S3S3. In July, the emission rate from S3S2 was significantly lower (*P*<0.03) compared to S3S3, which still had high emission rates of β-phellandrene, α-pinene, β-pinene and (1S)-Camphene (Fig. 10e,f). A similar difference between the trees was apparent in August as well where the emission rate from S3S2 was still significantly lower (*P*<.003) compared to S3S3 (Fig. 10g,h). The Norway spruce S3S3 was also found to emit the compound verbenone in August, a compound which could not be quantified in the study (Table 3).

The individual compound blend was also found to change over time for the healthy tree S3S3 as it was infested and when the infestation continued (Fig. A1). Before infestation, in total 10 compounds were identified, dominated by other BVOCs: decanal (28 %), nonanal (20 %), toluene (16 %) and 1,3,5-triflourobenzene (15 %) where the percentage represents the amount of the compound found in the sample relative to the total amount (Fig. A1). After bark beetle infestation started in June, the number of detected compounds increased to 27 and was now dominated by MTs ((1S)-Camphene (18%), 5-vinyl-m-xylene (15%) and β-phellandrene (9%); Fig. A1). The emissions during the campaign in July also consisted mainly of MTs with largest contributions from β-phellandrene (23 %) and β-pinene (22 %) followed by (1S)-Camphene (19 %) and α-pinene (16 %; Fig A1). The compound composition in August was similar as in June, with the majority of the blend consisting of MTs dominated by (1S)-Camphene, α-pinene and β-pinene (22 %, 13 % & 11 % respectively) and other BVOCs (2-methyl-1-phenylpropene (6%); Fig. A1).

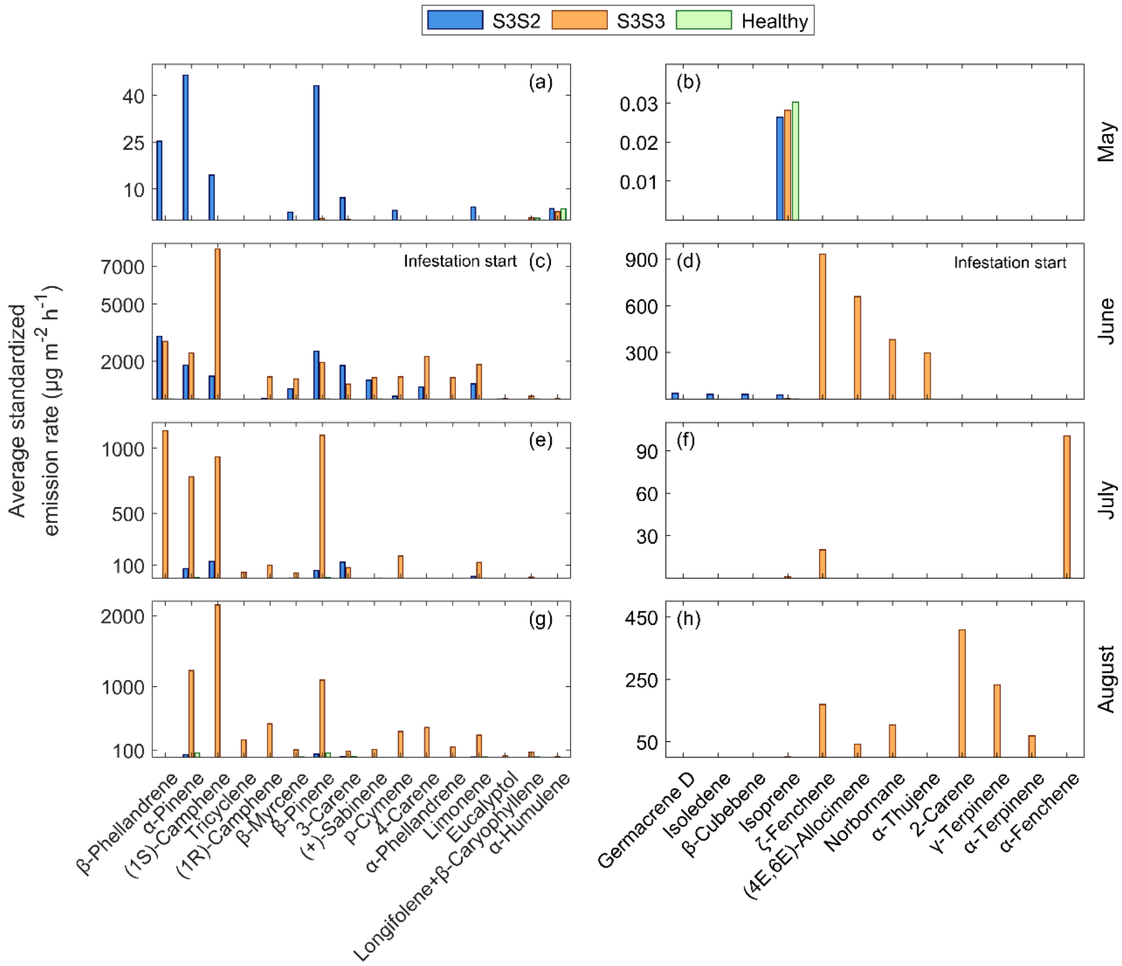

Figure 10: The average temperature standardized BVOC emission rates for all compounds from Norway spruce at plot 3 in Hyltemossa: infested spruce with ID S3S2 (blue), infested spruce with ID S3S3 (orange) and healthy trees (green). Measurements were taken in 2019 during (a,b) May, (c,d) June, (e,f) July and (g,h) August. The graphs are horizontally separated for visibility due to large differences in scale. The healthy trees are included in all graphs but the emission rates are not visible on the same scale as the infested trees in (c,d) June or (e,f) July. The bark beetle infestation had not started in (a,b) May, however, the spruce S3S2 was already subjected to stress from late bark beetle attacks during the previous season before the bark beetle infestation started again in (c,d) June, leading to higher emission rates already in May.

3.5 Reference emission rate at 30°C and calculated Q_{10} coefficient

From Eq. (5), the reference emission rate at 30°C (F_0) and the increase in emission rate with every 10°C (Q_{10} coefficient) were calculated for the healthy and infested Norway spruce trees from both sites. The result for emitted compounds show a Q_{10} coefficient ranging from 0.1 to 57 for healthy trees and 1 to 980 for infested trees where the Q_{10} coefficient increased for infested trees for all compounds but one, p-cymene (Table A2). The F_0 value, which indicates the emission rate at 30°C for each specific compound, also showed a difference between the healthy and infested trees. The spread of F_0 for healthy trees was ranging from 0.01 to 93 μg m^{-2} h^{-1} compared to 0.5 to 34,900 μg m^{-2} h^{-1} for the infested trees, however, compared to the Q_{10} coefficient, the F_0 value was higher for all compounds from the infested trees compared to the healthy (Table A2). The average Q_{10} coefficient for all compounds for healthy trees was 13 while it was 96 for infested trees, indicating a 7-fold increase of the Q_{10} coefficient. The average for F_0 was 21 μg m^{-2} h^{-1} for healthy trees and 2,650 μg m^{-2} h^{-1} for infested trees, a 127-fold increase, an increase which is in line with the increased emission rates when standardized according to G93 (Table A1). The highest increase in both Q_{10} and F_0 was seen in the compounds β-pinene and longifolene+β-caryophyllene with Q_{10} increasing 125-fold and 225-fold respectively, and F_0 increasing 3,160-fold and 2,100-fold respectively. The lowest change for Q_{10} was seen in α-pinene and p-cymene, where α-pinene had a 1-fold increase from healthy to infested and the Q_{10} coefficient for p-cymene actually had a 0.6-fold decrease for infested trees compared to healthy. Despite the lower Q_{10} coefficient for p-cymene in infested trees, its F_0 value was still higher for the infested trees, however, the increase of 5-fold was low compared to the other MT compounds. Isoprene was seen to have the overall lowest increase in F_0, increasing with 0.1-fold from healthy to infested. A significant difference was found for the Q_{10} coefficients for healthy and infested trees ($P<0.03$) as well as for F_0 ($P<0.01$).

There were four compounds for which the requirements for the calculations where only fulfilled for infested trees. Those where eucalyptol, tricyclene, (1R)-camphene and (+)-sabinene, for which an increase or comparison between healthy and infested trees cannot be made, but this might indicate that these compounds could be limited to emissions from infested trees only.

3.6 Calculated seasonal BVOC emissions from healthy Norway spruce bark and needles

The calculated needle emissions for the growing season of 2019 in Hyltemossa were found to vary with an average of around 60 to 170 µg m^{-2} h^{-1} for needle MT in July and August and an average of around 25 to 100 in May and 50 to 120 µg m^{-2} h^{-1} in September (Fig. 11b). Bark emissions were based on measured tree trunk temperature at 3m agl, averaged from 2 directions (North and East) and the average standardized emissions (*Ms*), 29 µg m^{-2} h^{-1} for MT and 2 µg m^{-2} h^{-1} for SQT, and the Q_{10} approach for healthy trees. The calculated emission rates from bark reached a maximum around 16 µg m^{-2} h^{-1} in July, which is ten times lower than the calculated needle emissions at the same time (Fig. 11c). The bark emission rates remained below 10 µg m^{-2} h^{-1} for most of the growing season. The estimated bark emission rates from healthy trees using the Q_{10} approach were generally about 5 µg m^{-2} h^{-1} lower than the calculated emission rates using the G93 approach, but steeply increased during the warmest days to match the G93-emissions (Fig. 11c).

For SQTs, the needle emissions peaked at 30 µg m^{-2} h^{-1} in late July at the same time as when MT emissions were high, and also showed emissions up to 20 µg m^{-2} h^{-1} earlier in June (Fig. A2b). For most of May and September, SQT emissions from needles were calculated to be below 5 µg m^{-2} h^{-1}. Bark emissions of SQT for healthy trees estimated with G93 were well below 1 µg m^{-2} h^{-1} throughout the season (maximum 0.75 µg m^{-2} h^{-1} in late July), and below 0.3 µg m^{-2} h^{-1} most of the time (Fig. A2c).

However, when comparing estimated bark emission from healthy trees with actual measurements of infested trees, bark emissions from infested trees were much higher (Fig. 11a). The measured bark MT emission rate from the infested tree reached up to around 18,000 µg m^{-2} h^{-1} as a daily average for one day, making the total MT emission rate (including needle emissions) increase by almost a 100-fold when the tree was infested. The lowest measured infested tree emission rate (around 3,900 µg m^{-2} h^{-1}) for MT was found during the July campaign, however, despite it being the lowest, it was still considerably higher than the MT emission rate from healthy trees of that day (70 µg m^{-2} h^{-1} including both needle and bark; Fig. 11). Bark MT emission rates from infested trees were at least around 55 times higher than the total MT emission rate from both needles and bark of a healthy tree.

For the SQT emission rates, the difference was not as distinct. The SQT emission rate reached maximum emission rate of around 0.75 µg m^{-2} h^{-1}, for bark emissions (Fig. A2b) and around 30 µg m^{-2} h^{-1} for needle emission (Fig. A2a) while the measured bark emission rate from the infested tree peaked around 40 µg m^{-2} h^{-1} as a daily average for one day, indicating a 1.3-fold increase when a tree is infested. The lowest measured infested tree emission rate was also in July for the SQTs, at around 1.4 µg m^{-2} h^{-1}, which was still higher than the calculated healthy bark emission rate at around 0.2 µg m^{-2} h^{-1}, but lower than the needle emission rate of about 5 µg m^{-2} h^{-1}.

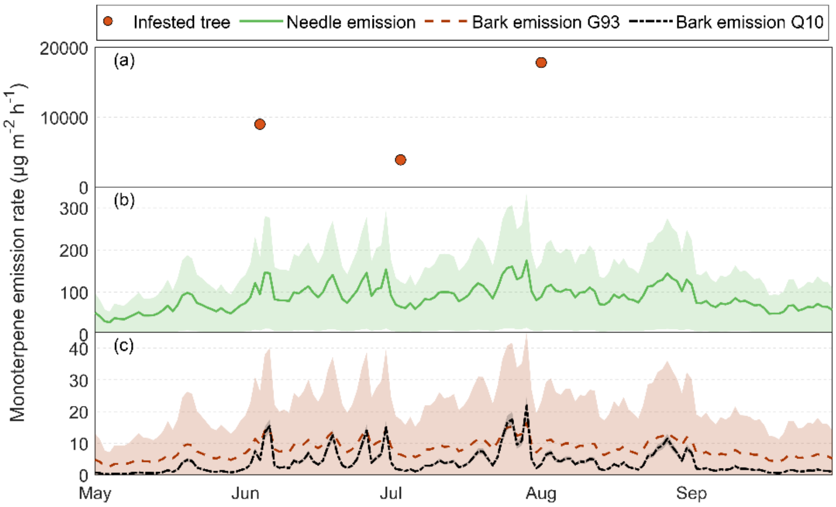

Figure 11. The measured and calculated BVOC emission rates for the group monoterpenes from Norway spruce in Hyltemossa: (a) the actual measured emission rates from infested Norway spruce bark (red dot), (b) calculated needle emission rates (green line) and (c) calculated healthy bark emission. The needle emissions were calculated based on the Guenther algorithm (Guenther et al., 1993) and the measured emission rates were taken from van Meeningen et al., (2017), specific needle area (SLA) was taken from Wang et al., (2017) and the air temperature at 24 m was taken from the HTM ICOS station (Heliasz, 2020). The healthy bark emission is calculated based on the tree temperature taken at 3 m height in the North and East orientation, data taken from the HTM ICOS station (Heliasz, 2020). The bark emissions are calculated using the Guenther algorithm (orange) and the Q_{10} temperature dependency (black) based on measured emission rates in this study. The shaded areas (green, orange and black shade) represent the standard deviation from the mean for the respective calculation method.

4 Discussion

4.1 Bark BVOC emissions from healthy or infested Norway spruce

Both emission rates and composition blend of bark BVOCs from Norway spruce trees were found to change when infested by spruce bark beetles, which is in line with previous studies on bark beetle infestation of conifer trees (Amin et al., 2013; Birgersson and Bergström, 1989; Ghimire et al., 2016; Heijari et al., 2011). In this study, 29 compounds unique to infested trees were identified from which the majority were MTs (n = 19; Table A1). Several of the identified compounds only emitted from infested trees were consistent with the findings of Ghimire et al. (2016), for example, eucalyptol, isoledene, (+)-camphor, tricyclene, α-phellandrene (Table A1). The findings in this study also show isoprene emission from both healthy and infested tree bark which initially was believed to originate from potential lichen cover as a study by Zhang-Turpeinen et al., (2021) found a positive correlation between isoprene and lichen cover. However, when visually evaluating bark photos for algae and lichen coverage there was no clear indication that higher coverage coincided with isoprene emissions making the origin of the isoprene emission uncertain. Ghimire et al. (2016) also assessed the lichen coverage and isoprene emission and their results are consistent with this study, they did not find any statistically significant relationship with isoprene emission from bark and lichen or algal cover.

The results of this study indicate a much greater increase in BVOC emission rates from healthy and insect infested conifer trees compared to previous findings (Amin et al., 2013; Ghimire et al., 2016; Heijari et al., 2011). In this study, the total Norway spruce bark BVOC emission rates was found to be 63- to 215-fold higher when a Norway spruce was infested compared to healthy, depending on how long the infestation had been ongoing (Fig. 6). Previous findings reported increases in emission rates up to 3-fold when Engelmann spruce (*Picea engelmannii*) was infested by spruce beetles (*Dendtoctunus rufipennis*; Amin et al., 2013), up to 10-fold when Scots pine (*Pinus sylvestris*) was infested by weevils (*Hylobius abietis*; Heijari et al., 2011) and up to 15-fold increase of emission rates from all BVOCs when comparing healthy Norway spruce trees with trees infested by the spruce bark beetle (Ghimire et al., 2016). The measured emission rates in this study are still 3 to 9 times higher than the emission rates in the study by Ghimire et al. (2016) with the highest increase comparing healthy and infested Norway spruce bark. As the emission rates in the study by Ghimire et al. (2016) are also standardized according to G93, temperature is not an impacting factor on the emission rates to create this large difference. A possible reason might however be the time since infestation start in relation to the measurements. An exponential decay in emission rates over time after infestation were found in this study (Fig. 8), suggesting that if measurements were taken early during the infestation the emission rates would be higher. However, the emission rates from exit holes (measured after 100 days) in this study are still higher than the emission rates found in June for Ghimire et al. (2016) originating from unspecified hole type. As they did not specify how long time the infestation had been ongoing it makes a comparison difficult as their June measurement could have originated from older infestations. In this study, measurements were taken throughout the growing season, from the same spruce, starting before the bark beetle infestations and from the very early infestation to later stages, something that, to our knowledge, has not been done before. Birgersson and Bergström (1989) did measure volatiles emitted from entry holes in bark beetle infested Norway spruce during the first week of infestation, but not longer.

The results from this study found emission rates from infested Norway spruce bark to decrease with time, similarly to what Eller et al., (2013) found when piercing holes in needles from Ponderosa pine (*Pinus ponderosa*). They found MT emission rates to increase by four orders of magnitude when the needle was pierced compared to undamaged needles and as the exposed resin hardened, the emission rates decreased exponentially until they reached similar levels as undamaged needles already after 30 days. In this study, induced emission rates from infested Norway spruce bark were seen to last up to 300 days before reaching similar levels as healthy bark, indicating the death of the tree (Fig. 8). This would suggest that the increased emission rates and their exponential decay over time is not only due to exposure of resin occurring as the spruce bark beetle first drill a hole, but also due to the developmental process of the beetle indicated by the visibility of the different hole types. This is supported by the fact that when comparing the total number of holes to emission rates for the individual Norway spruce trees, there was no distinct pattern (Fig. 9). However, when the holes were separated into entry and exit, it was apparent that entry holes generally have higher emission rates compared to exit holes (Fig. 9). This can also be supported by the result indicating higher emission rates at the start of an infestation (Fig. 8) when there is a majority of entry holes (Table 2). For the total BVOCs there is a large spread in emission rates, the second highest emission rate came from an individual (tree ID S3S2) at plot 3 in HTM that had less than 300 holes per square meter (Table 2) and mainly entry holes (Fig. 9). Some of the lowest emission rates came from an individual (tree

ID S1S1) with more than 1000 holes per square meter with mainly exit holes (Table 2). The same is true when looking at the compounds β-phellandrene, eucalyptol and β-pinene (Fig. 9). This result supports that the emission rates are linked to the time since infestation start.

The number of identified BVOC compounds found to be emitted from entry holes were higher compared to exit holes (Table 3), which further supports the assumption that the emission rates are due to ecological impacts of the spruce bark beetles and not only exposed resin. This is consistent with Birgersson and Bergström (1989) who looked at volatiles emitted from entry holes in bark beetle infested Norway spruce. They did however not look at exit holes, but their findings show that during the early stage of an attack, the MT emissions are high and the concentration of the collected MTs during the first day is consistent with what was found in this study 12 days after infestation. Two oxygenated MTs were found only from the entry holes which is consistent with the findings of Birgersson and Bergström (1989) and indicates emissions from the phloem. The bark beetle pheromones: germacrene D, isoledene, β-cubebene and 2-methyl-3-buten-2-ol (MB, not quantified) were also only found emitted from entry holes in this study – however, only from one tree (tree ID S3S2) and only during the June campaign (Fig. 10d). The presence of MB could be indicative of beetles in the galleries during the measurements of that individual tree (Birgersson et al., 1988; Zhao et al., 2011a). The high increase in emission rates could also be a result of bark beetle associated blue-stain fungus (*E. polonica*) as a study by Mageroy et al., (2020) found that inoculation with the fungus in Norway spruce bark was shown to increase the concentration of total terpenes 91-fold after 35 days compared to the concentration in healthy bark. They did however not measure the emission rates from the bark as done in this study, but their finding of high terpene concentration coincides with the high emission rates from infested Norway spruce bark found in this study.

4.1.1 Indications of differences in emissions from healthy or stressed trees during infestation

Two Norway spruce trees with different health status were selected at plot 3 in HTM to study if the health status might have an impact on induced tree emissions from bark beetle infestations. Prior to the infestation, we found that the emission rates were different; one tree (ID S3S3) had lower emission rates compared to the other (ID S3S2) which had significantly higher emission rates (Fig. 10a,b). The higher emission rates from S3S2 can be a sign of stress (Loreto and Schnitzler, 2010) and was not only visible in the BVOC emissions, but also from resin flow on the bark, supporting a theory that the high emission rates were caused by a late summer attack from spruce bark beetles during the previous season. In June, the two trees were subjected to spruce bark beetle infestation, S3S3 for the first time and S3S2 for the second time and 12 days into the infestation both trees showed induced emission rates (Fig. 10c,d). There was no significant difference in their respective emission rates; however, the trees were emitting slightly different compound blends, which might have been caused by the initial status of the trees. Tree S3S3 had mostly induced MTs of mainly (1S)-camphene, β-phellandrene, α-pinene and 4-carene but there were also emissions of ζ-fenchene, (4E,6E)-alloocimene, norbornane and α-thujene which were not found to be emitted from tree S3S2. Tree S3S2 was emitting several of the same MTs as S3S3 with the majority being emissions of β-phellandrene and β-pinene. But in addition to this, the previously mentioned bark beetle pheromones were found in the samples taken 12 days after infestation from this tree. The pheromones could indicate that there was ongoing blue stain fungi infection caused from the infestation that happened in the previous season or that the tree already had successful bark beetle infestation again (Birgersson et al., 1988; Zhao et al., 2011a). Previous studies have found that priming Norway spruce bark with methyl jasmonate (MeJA) as well as inoculating with blue-stain fungi have increased the spruce defense towards spruce bark beetles (Mageroy et al., 2020; Zhao et al., 2011a). As tree S3S2 had survived a previous infestation, a speculation can be that the tree also had fungi present during the new attack. However, the tree defense was not found to be increased but rather that the spruce bark beetles easily overtook it evident by visible entry holes, something which was found to be lower for trees when they are primed with MeJA or inoculated with fungi compared to healthy trees (Mageroy et al., 2020; Zhao et al., 2011a). Additional evidence for lowered defense of tree S3S2 is a comparison to the initially healthy tree's (S3S3) emission rates (Fig. 10): as the infestation continued, the emission rates from tree S3S2 were significantly lower compared to S3S3, an indication of decreased vitality of spruce S3S2 while tree S3S3 had induced emission rates until August indicating ongoing defense. The last measurement in August did however reveal occurrence of verbenone from the tree S3S3, which have been found to be emitted with successful fungal establishment and has been shown to repel bark beetles (Bakke, 2009; Cale et al., 2019). The findings of verbenone could indicate that the bark beetles had successfully overtaken the Norway spruce S3S3 in August, however, this could not be confirmed as the forest owner had to take down the trees which made further measurements impossible. As bark beetle outbreaks have been seen to increase in number, there might be an increase in the number of healthy trees being attacked and killed in addition to the typical attacks on already stressed trees (Jakoby et al., 2019). The results from this study revealed different blends of compounds when a tree was already stressed from previous infestation and attacked again compared to when the tree was healthy before the attack. Another important note on this is that the previously attacked tree (S3S2) indicated induced emission rates until the start of the next season (Fig. 10a,b), during which the tree was infested again with further induced emissions. The healthy tree (S3S3) did however have induced emission rates for longer when it was infested as healthy compared to when tree S3S2 was infested again. These results indicate that the second generation of spruce bark beetles, attacking late during the growing season, might lead to induced emission rates continuing until the next year. If a tree attacked late during the growing season survives, it can be attacked again the next season along with attacks on healthy trees. This might indicate that the initiation of a second generation of spruce bark beetles and the attack on healthy trees might have a larger impact on the total bark BVOC emission rates from Norway spruce where they are induced for longer.

The high BVOC emission rates from infested trees do not only affect the trees themselves, but ultimately they also impact atmospheric processes. Induced emission rates from BVOCs due to insect herbivory have been found to potentially increase SOA yields when modelling an increase in emission rates (Bergström et al., 2014). This would support the speculation that bark beetle induced BVOC emission rates are important to consider when modelling or measuring SOA formation. Taking not only the quantitative aspects of bark beetle induced emission rates into account, but also the qualitative effects, the SQTs α-humulene, longifolene and β-caryophyllene and MT α-pinene have been found to have highest SOA yield (Lee et al., 2006). This study found increased emission rates from longifolene+β-caryophyllene (quantified together) of around 54- and 20-fold from infested trees in the early and late season (Table 3). The MTs limonene and myrcene were slightly below the SQTs in ranking of SOA yield, and according to the findings in this study, they were seen to increase with an average of 50- to 170-fold and 30- to 530-fold respectively depending on the season, where the highest increase was in the early season. This change in compound blend could potentially lead to large impacts on SOA yield from bark beetle infested trees overall and highlights the importance of measuring and accounting for bark BVOC emissions.

In the comparison of the initially stressed tree and the initially healthy tree, it was apparent that there orignially was no significant difference in the total emission rate, but different compound blends were emitted. Linking this to SOA, the higher emissions of limonene and myrcene from the initially healthy tree early during the infestation indicates that higher SOA yields might come from healthy Norway spruce trees when infested. The high emission rates were also seen to continue until the trees were taken down in August implying that potential increase in SOA yield might continue for longer. Compounds unique to both infested trees were emitted as well, where the stressed tree emitted bark beetle related pheromones and the initially healthy tree emitted a broader blend of MTs, these individual compounds might play a role in the SOA yield as well. An increase of attacks on healthy trees might further affect the atmospheric processes, specifically production of SOA.

4.2 Bark beetle induced BVOC emissions in relation to other stresses, needle emissions and modelling

Significant increases of the temperature standardized BVOC emissions of Norway spruce bark were seen when trees were infested by bark beetles early in the season. Around a 230-fold increase in emission rate was seen for the group of MTs. This high increase in emission rate from insect stress for Norway spruce has not previously been observed according to the review by Yu et al. (2021), in which the highest recorded increase was around 2,000 %, including previous studies on spruce bark beetles. Heat stress was also identified as a stressor but it did not increase BVOC emissions as much as stress from bark beetles (Yu et al., 2021). A study on Norway spruce with air temperatures of 40 °C found that BVOCs increased by 175 % compared to emission rates at air temperature of 30°C (Esposito et al., 2016). This much lower than the increase in emission rates from bark beetle infestation found in this study. However, the impact of combined stresses from temperature and insect attacks might further increase the BVOC emissions. This is illustrated by the increase of reference emission rates after infestation across all BVOCs (F_0, Table A2) which are standardized at a reference temperature and therefore the difference between F_0 from healthy to infested trees could be interpreted as the change in stress induced BVOC emissions due to bark beetle attacks without the temperature effect. The temperature sensitivity as expressed by the Q_{10} coefficient was also found to increase for all compounds but one (of 15, namely p-cymene, Table A2) when trees became infested, indicating that the emission rates were accelerated by both a higher reference emission rate and an accelerated temperature response compared to healthy trees. This is however not the focus of this study, but as the BVOC compounds temperature sensitivity was found to increase when trees were infested, and as bark beetle infestations increased bark BVOC emissions more than any other comparable stress, there might be high influences of BVOC emissions from combined stress, making it important to account for when modelling the emissions.

The increase of bark emission rates seen in this study is high enough to considerably add to the emission rates of a full tree when comparing with emission rates from needles – which is considered the part of the tree with the highest emission rates. When modelling the emission rates, two approaches were used for the bark MT emissions, the G93 algorithm and the Q_{10} approach. The results showed similarities in pattern but the Q_{10} approach had larger increases in emission rates with higher temperature increase, something that was expected. The G93 modelled emission rates were constantly higher than the Q_{10}, and had less variability, which might be explained by the empirical coefficients used in the G93 compared to fitting F_0 and Q_{10} for each compound separately. For the needle emission rates, only G93 was used because of the light dependent nature of some BVOCs emitted from the needles that could not be explained by temperature in the Q_{10} approach only. The seasonal average emission rates from Norway spruce needles were measured during 2016 in Hyltemossa in a study by van Meeningen et al. (2017). As the study was conducted at the same site, their results were applied to this study as a comparison of bark BVOC emission to needle emission. It was clear that MT emissions from healthy bark does not compare to the needle emission (Fig. 11), where the seasonal average of the MT emissions where 11 times higher from needles than bark. However, when comparing seasonal average bark MT emission from infested trees with needle emissions it was the other way around: the bark emissions from infested trees where 6 to 20 times higher than the needle emissions depending on the time of season. The bark MT emission from healthy Norway spruce trees accounted for 8 % of the total emission rates from bark and needles. However, if there were an ongoing infestation from bark beetles, the bark emission rates would account for 95 % of the total emission rates during the early season, and 85 % during the late season. When comparing with the seasonal average of the emission rates from healthy trees, spruce bark beetle infestation could lead to a 6- to 20-fold increase in total emission rates from bark and needles depending on the season.

When a tree is infested, the emission rates increase significantly which can cause large local effects both for tree health and SOA production. The BVOC emission increase can also cause more widespread effects, if the outbreaks are sustained at high levels there would be large impacts regionally. During 2020 in Sweden, 8 million m^3 forest was affected by spruce bark beetles (Wulff and Roberge, 2020). This represents about 0.7 % of the total volume of Norway spruce trees with a diameter larger than 15 cm in Sweden (Skogsstyrelsen, n.d.). Using the seasonal average from the early and late season of the bark beetle infested emission rates of MT found in this study and the needle emission rates from van Meeningen et al. (2017), the infested trees during 2020 would contribute to an increase of about 4 to 13 % of total MT emission rate from Norway spruce trees in all of Sweden, including emissions from canopy and stem. The effects from insect herbivory and specifically spruce bark beetles might thus be underestimated both in emission and vegetation models (MEGAN, LPJ-GUESS; Guenther et al., 2006; Schurgers et al., 2009) and atmospheric chemistry models estimating BVOC impacts on oxidation capacity and SOA formation (ADCHEM; Roldin et al., 2011). Evident by the difference in emission rates during the early or late season, it is also important to consider the influence of time after infestation when modelling emission rates of BVOCs from infested Norway spruce to get a correct estimation of the spruce bark beetle impact.

5 Conclusion

Norway spruce trees are emitting BVOCs from the bark as a stress response to spruce bark beetles and as the number of spruce bark beetle outbreaks increase it will impact the total emission of BVOCs. The aim of the study was to examine how spruce bark beetles affect the BVOC emission rates from Norway spruce bark by looking at the difference between healthy and infested trees, the time after infestation start and the difference in emissions from different bark beetle drilled holes. One aim was also to provide an insight into how the BVOC emissions change from non-infested to infested, and following the infestation over time. The results show that there is a significant difference in BVOC emission rates from healthy and infested Norway spruce bark, but also a relationship between BVOC emissions from infested trees and the time after infestation start, which can be supported by results indicating a difference in emissions from bark beetle drilled entry and exit holes. The initiation of a second generation of bark beetles which can lead to late summer attacks, can potentially have prolonged impacts on the BVOC emissions as emission rates were found to be induced until the start of the next season. When the tree was infested again, the emission rates were further induced to reach the same levels as the induced emissions of a tree that was healthy before infestation. As the infestation proceeded, there was a difference in the emission rate and compound blend when comparing the initially stressed tree with the initially healthy tree, where the emission rates were induced to high levels until August for the initially healthy tree, but not for the initially stressed tree. Further studies are needed to support the findings and speculations of this study but also to analyze the entire impact of spruce bark beetles on Norway spruce trees. The importance of further studies is supported by the findings that the bark beetle induced BVOC emission rates can be considerably higher than previously thought and could potentially lead to a 1.1-fold increase of total MT emissions from Norway spruce in Sweden. Even further work would be needed in investigating the impact of coupled stress factors. A potential link between temperature stress and bark beetle stress was identified in this study, where trees seem to become more sensitive to temperature leading to potentially higher emission rates when temperatures increase in conjunction with bark beetle infestations. Based on the findings of this study, bark beetle infestations are believed to have higher impacts on the atmosphere and climate change than previously thought and samples from more trees and more frequently throughout the season are needed in order to fully understand the impact.

Appendix A

Table A1. Seasonal average temperature standardized emission rate (µg m^{-2} h^{-1} ± one standard deviation) from all Norway spruce trees located in Hyltemossa and Norunda. Presented are all the identified compounds, compound groups (Monoterpenes, sesquiterpenes and other BVOCs) and total emission emitted from healthy and infested (early and late season) Norway spruce bark. The increase or decrease (%) is presented for the infested trees as a change in emission rate from healthy to infested. The occurrence (%) indicates how often each compound appeared in the samples. The compounds that were identified but unable to quantify is presented as n.q. (no quantification).

	Healthy		**Infested early season**			**Infested late season**		
Compound name	*average ± std (µg m^{-2} h^{-1})*	*occurrence (%)*	*average ± std (µg m^{-2} h^{-1})*	*increase (%)*	*occurrence (%)*	*average ± std (µg m^{-2} h^{-1})*	*increase (%)*	*occurrence (%)*
Monoterpenes	29 ± 51		6,600 ± 6,700	22,400		1,900 ± 1,300	6,500	
α-pinene	12 ± 20	76	910 ± 1030	7,800	100	820 ± 890	7,100	100
β-pinene	8 ± 19	56	950 ± 960	11,500	100	230 ± 170	2,600	100
3-Carene	3 ± 5	49	290 ± 420	11,400	100	30 ± 40	1,200	95
Limonene	2 ± 3	44	320 ± 320	16,900	88	90 ± 80	4,400	100
p-Cymene	1 ± 1	40	240 ± 320	49,200	63	50 ± 40	10,700	77
β-Myrcene	0.3 ± 0.8	18	160 ± 170	49,800	79	10 ± 6	1,900	86
β-Phellandrene	3 ± 8	11	670 ± 660	24,800	44	190 ± 160	6,900	68
(1S)-Camphene	2 ± 6	6	1,520 ± 1,970	89,100	75	390 ± 230	22,800	100
2-Cyclopentylcyclopentanone	n.q	4	-	-	-	n.q	-	5
α-Terpineol	n.q	3	-	-	-	-	-	-
5-Ethyl-m-xylene	n.q	1	-	-	-	-	-	-
(+)-Sabinene	0.1 ± 0	1	210 ± 200	257,900	44	3 ± 0	3,600	5
(1R)-Camphene	-	-	190 ± 740	-	19	110 ± 80	-	77
Tricyclene	-	-	170 ± 250	-	50	20 ± 20	-	36
Eucalyptol	-	-	10 ± 20	-	44	2 ± 5	-	27
(+)-Camphor	-	-	-	-	-	n.q	-	46
Pinocarvone	-	-	n.q	-	44	n.q	-	5
4-Carene	-	-	350 ± 280	-	38	-	-	-
ζ-Fenchene	-	-	120 ± 190	-	25	1 ± 0	-	5
α-Phellandrene	-	-	110 ± 200	-	31	-	-	-
(1R)-(-)-Myrtenal	-	-	n.q	-	31	-	-	-
(4E,6E)-Allocimene	-	-	50 ± 80	-	25	-	-	-
5-Vinyl-m-xylene	-	-	n.q	-	25	-	-	-
3-Pinanone	-	-	-	-	-	n.q	-	14
Norbornane	-	-	60 ± 80	-	19	-	-	-
γ-Terpinene	-	-	90 ± 0	-	13	-	-	-
α-Fenchene	-	-	10 ± 0	-	13	-	-	-
2-Carene	-	-	160 ± 0	-	13	-	-	-
α-Thujene	-	-	20 ± 0	-	13	-	-	-
Verbenone	-	-	n.q	-	13	-	-	-
Myrtenal	-	-	n.q	-	6	-	-	-
α-Terpinene	-	-	30 ± 0	-	6	-	-	-
Sesquiterpenes	2.1 ± 3.2		53 ± 74	2,400		18 ± 24	700	

Longifolene+β-Caryophyllene	0.7 ± 1.4	18	38 ± 70	5,300	56	14 ± 24	1,800	55
α-Humulene	1.4 ± 3	48	5 ± 9	200	31	4 ± 13	200	18
Germacrene D	-	-	4 ± 0	-	19	-	-	-
Isoledene	-	-	3 ± 0	-	19	-	-	-
β-Cubebene	-	-	3 ± 0	-	19	-	-	-
Other BVOCs	0.4 ± 0.9		3.4 ± 6.7			0.1 ± 0.2		
Isoprene	0.4 ± 0.9	58	3 ± 7	700	63	0.1 ± 0.2	-65	27
Decanal	n.q	45	n.q	-	13	n.q	-	14
Benzene	n.q	45	-	-	-	n.q	-	14
Nonanal	n.q	39	n.q	-	6	n.q	-	14
Toluene	n.q	21	n.q	-	6	n.q	-	9
1,3,5-Trifluorobenzene	n.q	14	-	-	-	-	-	-
Benzaldehyde	n.q	12	-	-	-	n.q	-	9
Butyl formate	n.q	8	-	-	-	n.q	-	5
Caprolactam	n.q	7	-	-	-	-	-	-
Cyclopentanone	n.q	5	-	-	-	n.q	-	9
Methanesulfonic anhydride	n.q	5	-	-	-	n.q	-	5
Trimethylbenzol	n.q	2	-	-	-	-	-	-
m-Xylene	n.q	2	-	-	-	-	-	-
Ethylhexanol	n.q	2	-	-	-	-	-	-
Acetic acid	n.q	2	-	-	-	-	-	-
tert-Butylamine	n.q	1	-	-	-	n.q	-	9
m-Ethyltoluene	n.q	1	-	-	-	-	-	-
o-Ethyltoluene	n.q	1	-	-	-	-	-	-
Methyl 3-hydroxy-2,2-dimethylpropanoate	n.q	1	-	-	-	-	-	-
1-Pentene	n.q	1	-	-	-	-	-	-
Butanal	n.q	1	-	-	-	-	-	-
1-Nonene	n.q	1	-	-	-	-	-	-
Isobutenyl methyl ketone	n.q	1	-	-	-	-	-	-
Diacetone alcohol	n.q	1	-	-	-	-	-	-
Furfural	n.q	1	-	-	-	-	-	-
1,6-Anhydro-β-d-talopyranose	n.q	1	-	-	-	-	-	-
dl-3,4-Dehydroproline methyl ester	n.q	1	-	-	-	-	-	-
6,10,14-Trimethyl-2-pentadecanone	n.q	1	-	-	-	-	-	-
Undecanal	n.q	1	-	-	-	-	-	-
Carbon disulfide	n.q	1	-	-	-	-	-	-
2-Methyl-1-phenylpropene	-	-	n.q	-	38	n.q	-	9
2-Methyl-3-buten-2-ol	-	-	n.q	-	19	-	-	-
Benzoic acid	-	-	-	-	-	n.q	-	9
Acetophenone	-	-	-	-	-	n.q	-	9
Methyl acetate	-	-	-	-	-	n.q	-	9
(-)-Bornyl acetate	-	-	n.q	-	13	-	-	-
Bornyl acetate	-	-	n.q	-	13	-	-	-

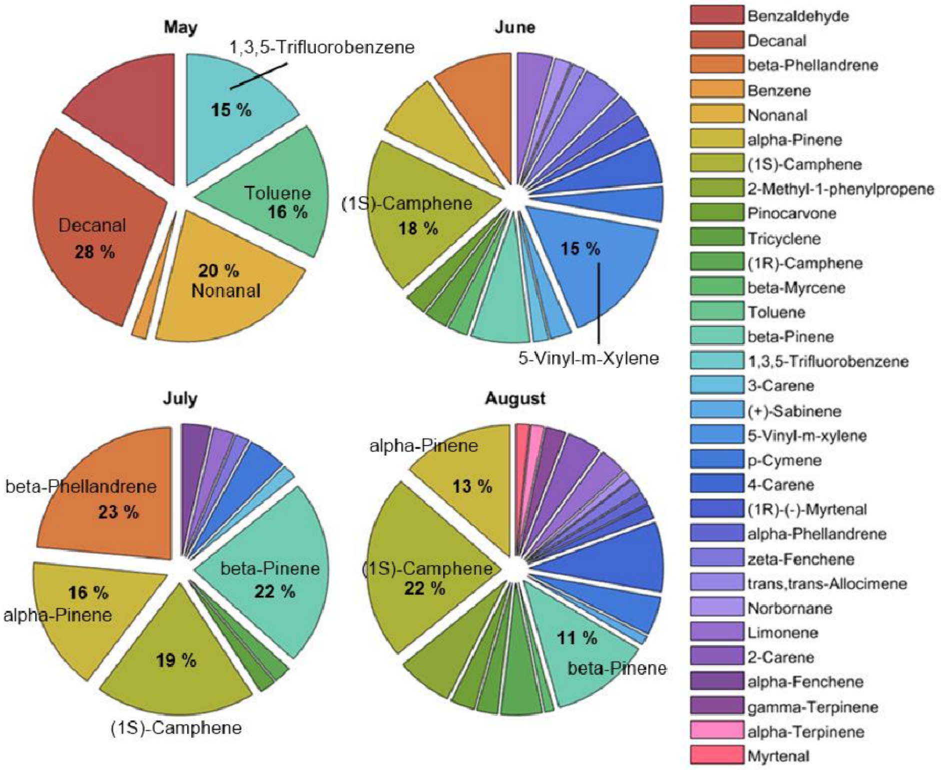

Figure A1: The daily average blend from the Norway spruce S3S3 and percentage contribution in mass throughout the summer (May, June, July and August), showing only compounds with a mass contribution of at least 1 %.

Table A2. The difference between healthy and infested trees when applying the calculations for the Q_{10} temperature dependency. F_0 is the reference emission rate standardized at 30 °C. The Q_{10} coefficient indicates the emission rate change for every 10 °C temperature difference and is therefore a measure of temperature sensitivity.

	F_0 (µg m^{-2} h^{-1})		Q_{10}	
Compound name	*Healthy*	*Infested*	*Healthy*	*Infested*
Monoterpenes				
β-pinene	11	34,900	8	980
(1R)-Camphene	-	1,500	-	80
β-Phellandrene	21	1,240	3	38
α-pinene	55	880	19	19
(1S)-Camphene	93	470	6	14
β-Myrcene	16	250	57	170
Limonene	13	120	12	17
3-Carene	5	110	7	26
p-Cymene	16	90	22	15
Tricyclene	-	80	-	14
(+)-Sabinene	-	70	-	8
Eucalyptol	-	3	-	3
Sesquiterpenes				
Longifolene+β-Caryophyllene	0.01	24	0.1	33
α-Humulene	0.01	0.5	0.7	1

Other BVOCs				
Isoprene	1	2	10	24

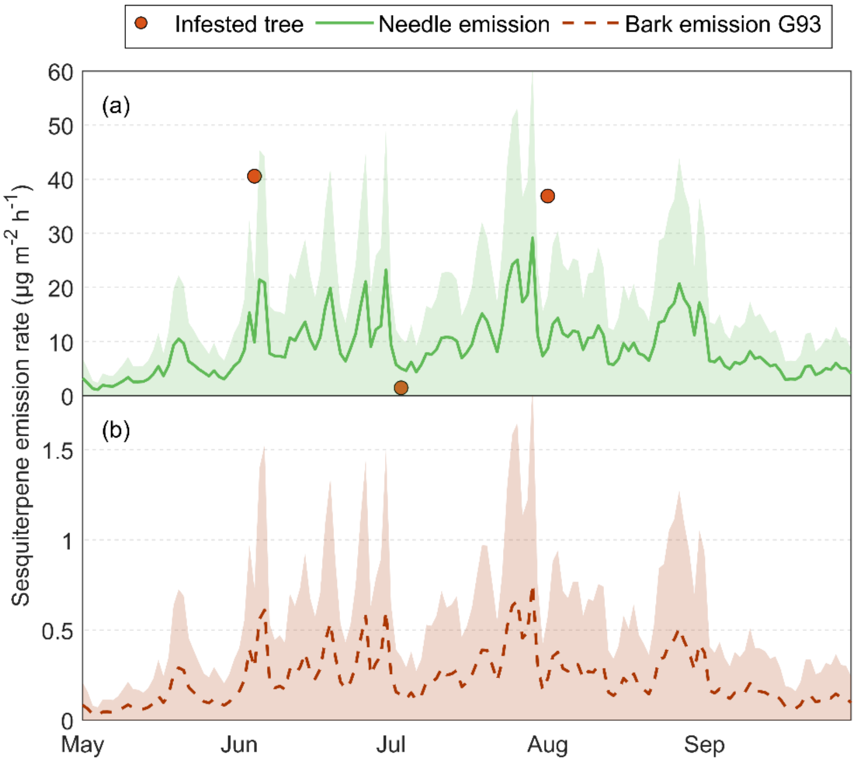

Figure A2. The measured and calculated BVOC emission rates for the group sesquiterpenes from Norway spruce in Hyltemossa: (a) the actual measured emission rates from infested Norway spruce bark (red dot) and calculated needle emission rates (green line) and (b) calculated healthy bark emission. The needle emissions are calculated based on the Guenther algorithm (Guenther et al., 1993) and the measured emission rates are taken from van Meeningen et al., (2017) and specific needle area (SLA) was taken from Wang et al., (2017), using the air temperature at 24 m taken from the HTM ICOS station (Heliasz, 2020). The healthy bark emission is calculated with the Guenther algorithm (orange) based on the tree temperature taken at 3 m height in the North and East orientation using data taken from the HTM ICOS station (Heliasz, 2020). The shaded areas (green, orange and black shade) represent the standard deviation from the mean for the respective calculation method.

Author contribution

EJ and TH designed and planned the campaigns. EJ performed the measurements. EJ performed the data analysis with contributions from KL, AG and AMJ. Funding was acquired by TH. EJ prepared the manuscript draft with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

The authors would like to thank the ICOS Hyltemossa and Norunda staff for logistical support and Gustafsborg Säteri AB and Mats de Vaal for support with forest sites and tree selection. We would also like to thank Julia Iwan, Marieke Scheel, Tanja Sellick and Emily Ballon for assistance with field measurements and Cleo Davie-Martin for valuable discussions on sample analysis. The research presented in this paper is a contribution to, and was supported by the Strategic Research Area Biodiversity and Ecosystem Services in a Changing Climate, BECC (BECC.LU.SE), funded by the Swedish government.

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