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

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10 **Abstract**

Biogenic volatile organic compound (BVOC) emissions from trees subjected to biotic stress are higher compared to healthy trees and they may also have a different compound composition. This in turn affects atmospheric chemistry and can lead to either a positive or a negative feedback to the climate. Climate change favours the abundance of the European spruce bark beetle (*Ips typographus*) which attacks the bark of Norway spruce (*Picea abies*) trees causing induced BVOC emissions from the trees as a response to the insect stress. Here, results are reported from a study analyzing the difference in emission rates between healthy and bark beetle-infested Norway spruce trees, changes in emissions rates over time since the infestation started, and differences in emission rates from bark beetle drilled entry and exit holes.

20 Bark chamber measurements on both healthy and infested trees were performed during the summer of 2019 at Hyltemossa and Norunda research stations in Sweden. The measurements showed that induced BVOC emissions following the bark beetle infestation were dominated by entry hole emissions in the early growing season and exit hole emissions in the later season. The results showed a significant difference in emission rates between healthy and infested trees during both seasons. The seasonal average standardized BVOC emission rate 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} ± 6,900 µg m^{-2} h^{-1} and 2000 µg m^{-2} h^{-1} ± 1,300 µg m^{-2} h^{-1} during the early and late season respectively. BVOC emission rates were highest at the start of the infestation and decreased exponentially with time showing induced emission rates for up to one year after which the emission rates were similar to those from healthy bark. Constitutive needle emission rates from healthy trees were found to be 11 times higher than bark emissions from healthy trees. However, when Norway spruce trees were infested, the bark emission rates were instead 6 to 20 times higher than the needle emissions causing substantial increases in the total tree BVOC emission rate. This could lead to high impacts on atmospheric processes, specifically the formation of secondary organic aerosols which have a higher yield from some monoterpene compounds, which increased from infested trees.

1 Introduction

35 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 forest volume killed by spruce bark beetles in a single year in Sweden. On average, between 1990-2010, around 150,000 m^3 of 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 increased risks of storm felling and drought weaken the trees making them more vulnerable to bark beetle infestations (Jönsson et al., 2012). Higher temperatures and a longer growing season may 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 and outbreaks that can cause extensive damage to spruce forests (Jakoby et al., 2019; Seidl et al., 2014).

Biogenic volatile organic compounds (BVOCs) emitted from trees have many functions, including a defense system against heat and oxidative stress (Loreto and Schnitzler, 2010). The compounds 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) and oxidized products from emitted BVOC can be important drivers for the formation of secondary organic aerosols (SOA; Kulmala et al., 2003). Plants normally emit a certain BVOC species composition, however, stress on the plants might affect the composition and change the BVOC's oxidation capacity in the atmosphere leading to more efficient SOA precursors which stimulate 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 that are highly efficient precursors of SOA. There are thus high uncertainties regarding the BVOC emission contribution to either a negative feedback to the climate (enhancing cloud formation and radiation scattering (Paasonen et al., 2013)) or a positive feedback (via increasing tropospheric ozone levels (Arneth et al., 2010; Jia et al., 2019)).

Constitutive BVOCs are emitted from all parts of Norway spruce, with the bark surface and trunk emissions suggested to contribute a lot more to the whole tree emissions than previously thought, even when not attacked by bark beetles (Greenberg et al., 2012). High amounts of different BVOCs are stored in plant tissues and are used to fight off predators during herbivory (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). As the parental bark beetles attack Norway spruce trees by drilling through the bark and excavating egg galleries in the phloem, the spruce tries to prevent this by submerging the parental bark beetles and egg galleries with resin, containing compounds toxic to spruce bark beetles such as myrcene and α-terpinene (Celedon and Bohlmann, 2019; Everaerts et al., 1988; Krokene, 2015). This can potentially kill the beetles or push them out through the entry holes (Raffa, 1991). The resin is the main part of the spruce defense and contains high concentrations of BVOCs that volatilize when the resin flows out of the tree, causing it to harden and close the wound. 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) and the 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). If the spruce could not successfully defend itself and larvae develop in the galleries, a the new generation of spruce bark beetles will start to leave the tree after about eight weeks by drilling exit holes through the bark resulting in decreased tree vitality (Öhrn et al., 2014).

The defense mechanisms of Norway spruce are still not fully known or understood, and only a few studies have analyzed the BVOC trunk emissions induced by an attack by the European spruce bark beetle (Ghimire et al., 2016; Zhao et al., 2011b). This study aimed to: (i) investigate the impact of spruce bark beetle infestation on BVOC emissions and the emitted compound composition from Norway spruce trunks, (ii) study the changes in BVOC emission rates and compound composition with the number of holes drilled by the bark beetles, and (iii) to track the compound emissions and composition over time. The final aim (iv) was to compare and relate the spruce bark beetle induced BVOC emission rates to needle emissions to see how important bark emissions are in the ecosystem perspective. Based on previous findings, three hypotheses were formulated: (H1) infested trees have higher bark emission rates than healthy trees and infestation changes the compound composition, (H2) BVOC emission rates are highest at the start of an infestation and decrease over time in response to declining tree vitality and eventual death of the tree, and (H3) BVOC emission rates are affected by the specific bark beetle drilled hole type (i.e. entry or exit hole), where the emission rates from entry and exit holes differ because of a difference in defense activity of the spruce.

2 Methods

2.1 Site description

Field work was carried out between beginning of May and late August 2019 at three plots in managed forests at the ICOS (Integrated Carbon Observation System, ICOS-Sweden.se) research station in Hyltemossa (HTM, 56°06′N, 13°25′E; Fig. 1a) and at two plots in the managed forest at the ICOS research station in Norunda (NOR, 60°05′N, 17°29′E; Fig. 1c; Table 1). The field sites were located in southern and central Sweden (Fig. 1b). The forest in HTM was dominated (>97% of the species composition) by Norway spruce with a small fraction (<3%) of Scots pine (*Pinus sylvestris*) and deciduous trees. The understory vegetation was sparse, containing mostly mosses (Heliasz et al., n.d.). The forest in NOR was dominated by Norway spruce (54%) and Scots pine (37%) with a small fraction (9%) of deciduous trees and understory vegetation with shrubs of mostly blueberries, cranberries, mosses and flowers (Mölder et al., n.d.). In HTM the trees were around 40 years old with an average height of 19 m in 2019 and NOR had 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).

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 the availability of bark beetle infested trees inside the forest plantation. At HTM, the three plots were visited five times during the summer, and at NOR the two plots were visited once (Table 1). Five Norway spruce trees were selected at plot 1 in HTM and four trees at plot 2 and 3 in HTM (total n = 13 in HTM) and were measured repeatedly throughout the season. Three trees were selected at each plot in NOR (n = 6) and only measured once. In total 19 trees were measured (Table 1). Healthy trees (n = 11) at HTM were selected by visual examination in close contact with the forest manager employed by the forest owner, Gustafsborgs Säteri AB, in May 2019. Trees that were potentially stressed by forestry machinery or pests were not selected for the study. The infested trees (n = 9) 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 (Fig. 1a). These trees were selected for the study to analyze long-term infestation effects. An active spruce bark beetle outbreak was occurring in NOR in 2019 and only infested trees were selected at that site to expand the sample size for the infested trees.

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Table 1. Timetable of the sampling conducted during 2019 at the sites Hyltemossa (HTM) and Norunda (NOR). Indicated is the number of collected samples during each field visit where n indicates the number of Norway spruce trees by category (healthy or infested) at each plot. Note that one of the healthy spruce trees at plot 3 was infested in June and thus changed the number of healthy and infested trees at that plot (number in brackets) while the total number remained at 19.

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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	
			n = 4	n = 1	n = 4	n = 0	n = 3 (2)	n = 1 (2)	n = 0	n = 3	n = 0	n = 3	n = 19
May	4th-6th	HTM	9	3	12	-	12	-					36
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
Total									Healthy = 144, Infested = 40, Total 184				
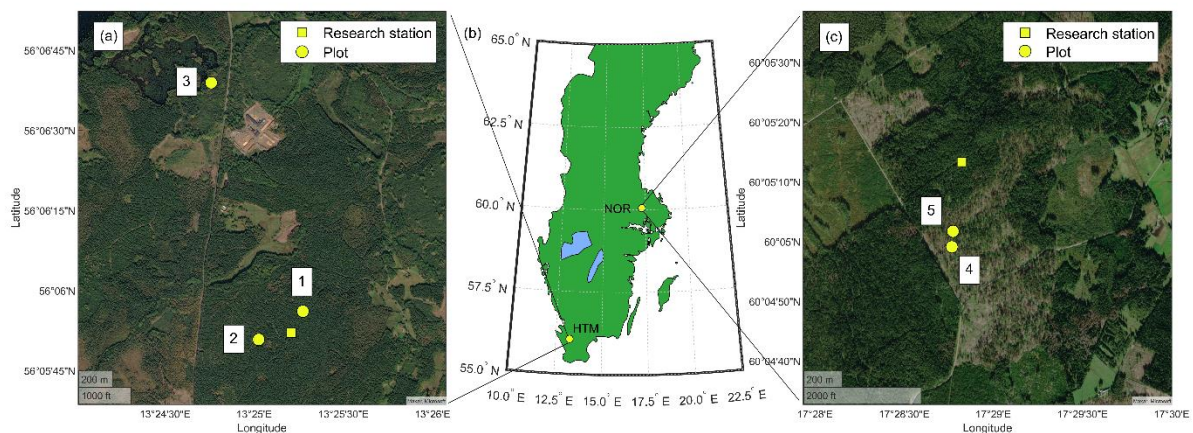
Figure 1: The location of the study site Hyltemossa (HTM; a), the location in Sweden (b) and site Norunda (NOR; c). Measurement plots (yellow circle) at HTM (1-3) and NOR (4-5) are shown in the site-specific maps and their location
135 **relative to the ICOS station (yellow square). Healthy Norway spruce trees were measured in plot 1-3 and infested spruce trees were measured in plot 1, 3, 4 & 5. The figure was created in MATLAB and Mapping Toolbox release 2021a (The MathWorks, Inc., Natick, MA, USA).**

A bark beetle slit trap with pheromones was installed at plot 3 in HTM as an attempt to attract bark beetles to the
140 plot. The trap was installed between May and June (Table 1) using one bag of biological attractant containing the pheromone 2,3,2 Methylbutenol (Typosan P306, Plantskydd AB, Ljungbyhed, Sweden). This resulted in infestation of two trees, one initially healthy tree (ID S3S3, Table 2) and one with signs of late bark beetle infestation from the preceding season (ID S3S2, Table 2), allowing us to monitor the infestation development. The two trees were included in the repeated measurements taken throughout the season and used as a case study
145 allowing us to monitor the infestation development from the beginning of the infestation until the trees were taken down by the forest owner as a precautionary measure to protect the neighbouring stands from infestation.

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) at HTM and 14.2 °C (± 4.2 °C) at NOR with the sum of the precipitation over the growing season being 168 mm at HTM and 151 mm at 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 of up to 3 mm (Fig. 2). In HTM, it was coldest (1 °C to 11 °C) in May and warmest (12 °C to 28 °C) in June.
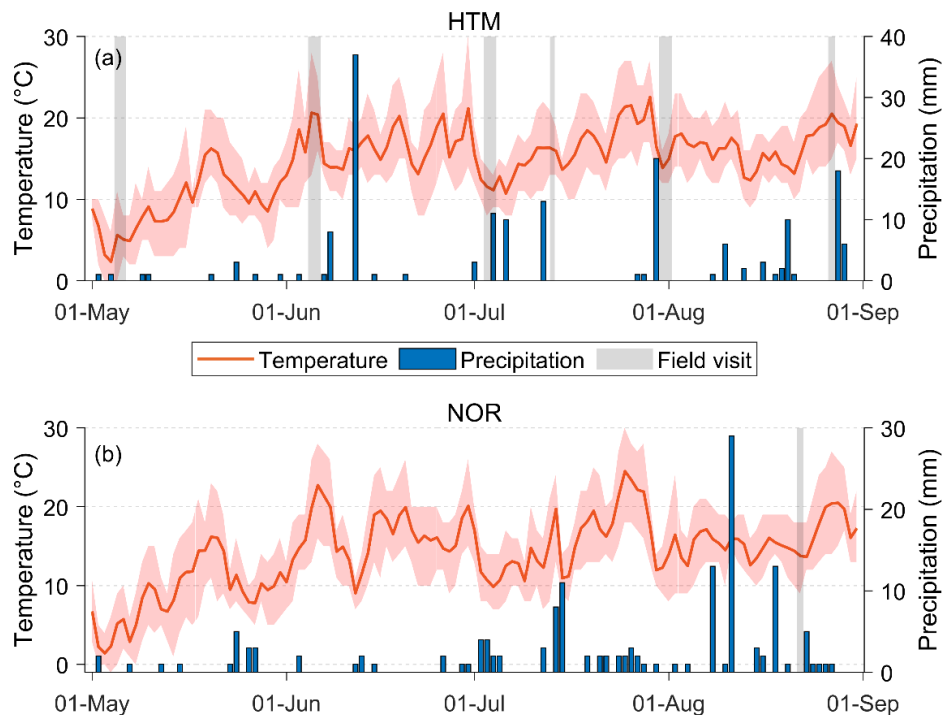
Figure 2: The daily average temperature (red line) with daily minimum and maximum temperature (red shade) and total daily precipitation (blue bars) for the study sites in (a) Hyltemossa and (b) Norunda. The field visits are marked in grey. The weather data was acquired from the ICOS research stations 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., Orangeburg, NY, USA). The pump box system was used to purge the trunk chamber of 0.6 to 0.9 L volume with air at a flow rate of 0.7 lpm (litres per minute; Fig. 3). A BVOC filter (Hydrocarbon trap, Alltech, Associates Inc., Chicago, IL, 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 itself 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) polyamide 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.

During the field visits, trees from one plot were sampled three times 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 the build-up of BVOCs inside the chambers. The bark temperature was measured with an infrared thermometer (IRT260, Biltema, Sweden) at four different points inside the chamber before the sampling, after which the lid was fastened and the chamber was purged with air for 15 minutes before sampling started. The air temperature inside the chamber was measured at the start and the end of the BVOC collection. 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 observed during the field visit in June (Table 1). For the other plots, the swarming time was retrieved using data from Swedish Forest Agency's (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 the main swarm in NOR around week 20-21 for 2019 (Fig. S2)

The number of bark beetle holes inside the chamber was counted before each measurement and lichen and algal cover was assessed. Entry and exit holes were separated based on photographs of the bark inside the chambers of the infested trees (Fig. 4). The entry and exit hole separation was based on the characteristics of the hole, where entry holes had more resin bleed compared to exit holes, which also had a rounder shape. The number of holes counted inside the chamber area of each infested tree during the field visits is listed in Table 2 along with an extrapolation of the counted holes from the chamber area to one square meter of 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 the estimated start of infestation. As the entry and exit holes consistently occurred before or after 100 days since infestation started, the measurements with mainly entry holes are referred to as the 'early season' and the measurements with mainly exit holes as the 'late season'.
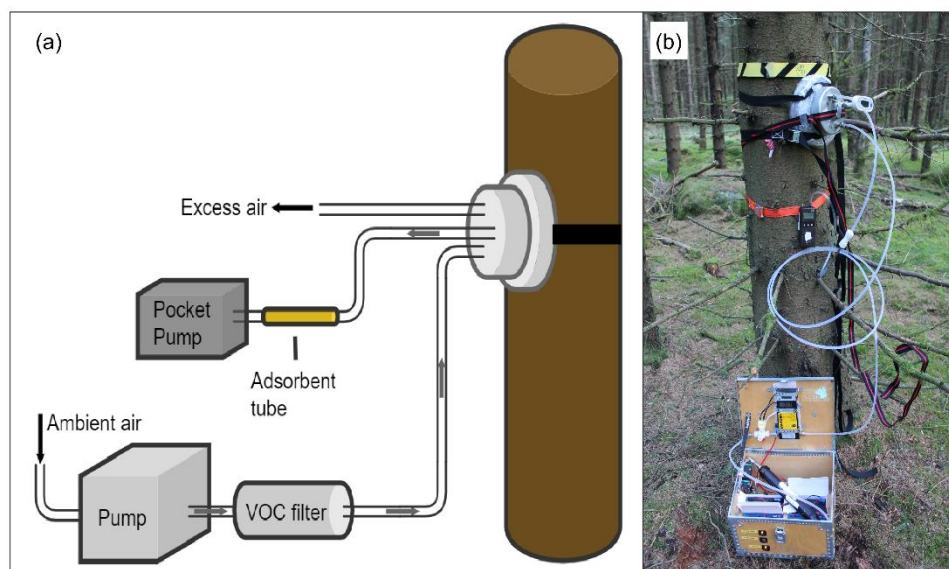
Figure 3: The experimental setup (a) and a field photo (b) of the tree trunk chamber mounted on a Norway spruce trunk. The chamber is connected to a pump box used to provide BVOC- and O₃-free purge air. The BVOC samples were collected with adsorbent tubes by extracting the air from the chamber using a pocket pump.
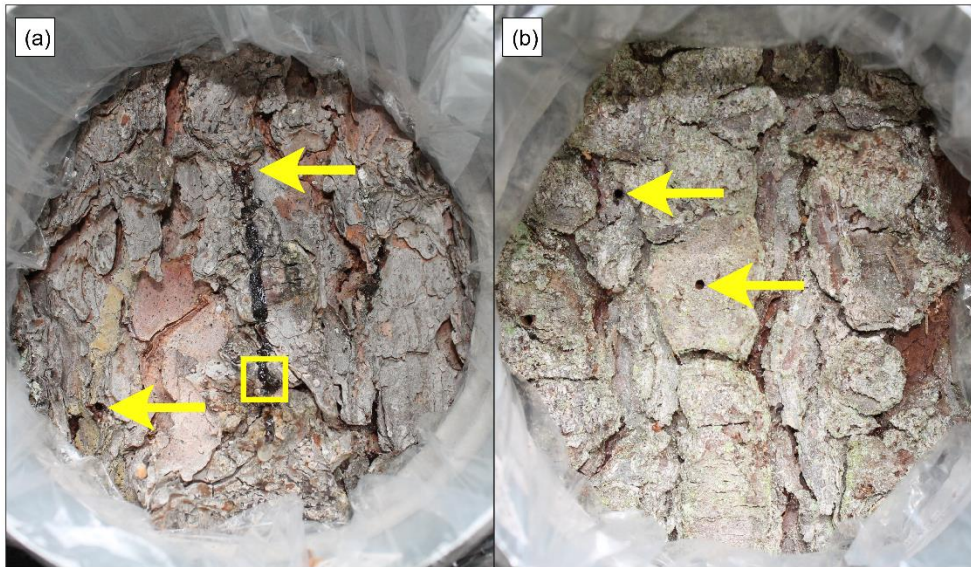
Figure 4: Examples of infested Norway spruce trees with (a) entry and (b) exit holes. The arrows indicate examples of bark beetle drilled holes and the square box frames a bark beetle. There are more holes in the pictures than indicated by the arrows.

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Table 2. The infested Norway spruce trees (n = 9) by tree ID, site, plot and the number of holes counted inside the chamber at the given date of the field visit for each tree. The counted holes were upscaled to holes per square meter of bark surface and the majority of the hole type was defined to be either mostly entry or exit holes. The bark of the Norway spruce with the ID S1S1 was infested during the late season of 2018 and had thus already a majority of exit

215 **holes early in 2019.**

Tree ID	Site	Plot	Date	Number of holes inside the 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 184 samples were taken, where 144 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

220 adsorbents Tenax TA (a porous organic polymer) and Carbograph 1TD (graphitized carbon black) were used to sample BVOCs 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 total volume for each sample was between 5 to 6 L. The method was repeated throughout the day until all trees of that plot were measured three times. Blank samples were collected from the chamber inlet air twice

225   per day, once before the first sample and once after the last sample to capture possible background contamination.

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) heating

230   the cartridges to 280 °C in a flow of purified helium (He, ALPHAGAZ 1, Air Liquide Gas AB, Sweden) for 10 minutes 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 then 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 the carrier gas to a gas chromatograph-mass spectrometry system (GC-MS, Shimadzu QP2010 Plus, Shimadzu

235   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,

240   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 in 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 were coeluted in the chromatography and are therefore presented

245   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). The detection limit was set to 0.4 ng in the analysis software based on the analysis of blank samples.

250   Outliers in the BVOC samples were found from 12 measurements of Norway spruce trees located at plot 1 and 2 in HTM (Fig. 1a). The bark was examined with bark photos, and it was detected that the chamber in those 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

255   discovering placements on top of a bark hole likely not originating from spruce bark beetles, and thus not suitable for this study. Four samples were also lost during analysis and could not be used for the study. A total of 33 samples were removed resulting in a total of 151 samples used whereof 113 were from healthy trees and 38 from infested.

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})

260   according to Eq. (1), following Ortega and Helmig (2008):

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

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

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

Finally, the ER was extrapolated to one square meter of bark surface, ER_{sqm}, based on the number of holes within

270 the chamber and the chamber's bark area according to Eq. (3):

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

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

275 a difference in number 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):

280 $$M = M_S \cdot e^{(\beta(T-T_S))}, \tag{4}$$

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.

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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

290 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):

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

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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

300 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 were 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 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 that data was not normally distributed. Statistical analyses 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 difference in emission rates from the healthy trees at plot 1, 2 and 3 in HTM was tested. To evaluate the study hypotheses, we tested the difference in emission rates from healthy and infested trees from all plots and sites (H1), the difference between the calculated Q_{10} coefficient and F_0 for the healthy and infested trees (aim (iv)), emission rates from infested Norway spruce and the evolvement over time (H2) and finally, emission rates from infested Norway spruce and the number and type of bark beetle holes (H3).

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):

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

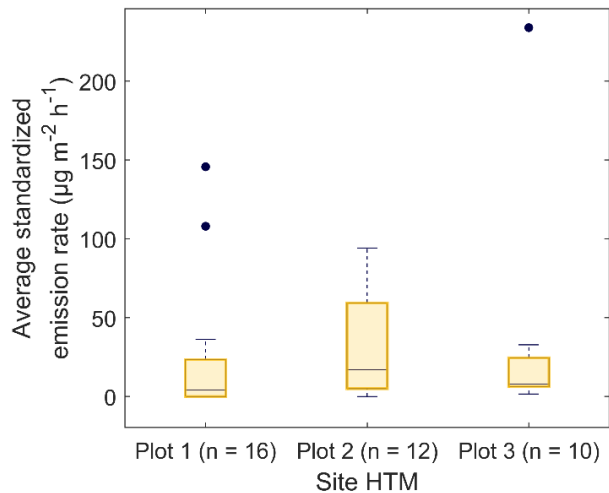
where x is the emission rate in µg m^{-2} h^{-1}.

3 Results

3.1 Bark BVOC emissions from healthy and infested Norway spruce

For the healthy Norway spruce trees in HTM, the average temperature standardized bark BVOC emission rate for all compounds 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 all samples from the healthy spruce bark with an average emission rate of 0.4 ± 0.9 µg m^{-2} h^{-1} (Table 3). When the healthy trees were separated into early and late season, there was no significant difference in their respective emission rates (early season: 29 ± 52 µg m^{-2} h^{-1} and late season: 37 ± 44 µg m^{-2} h^{-1}, $P>0.4$, Fig. 6).

The variability of the emission rates from healthy trees differed little between the plots in HTM. The standardized emission rates ranged 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 rates 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.

345 **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 temperature standardized emission rates ($P>0.3$).**

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For the bark beetle infested trees at both sites (HTM and NOR), the average temperature standardized emission rate for all BVOCs was $6,700 \pm 6,900$ µg m^{-2} h^{-1} (mean ± standard deviation; Table 3) for the early season (n = 6). The average for trees infested in the late season (n = 8) was $2,000 \pm 1,300$ µg m^{-2} h^{-1} (Table 3). MTs was the most

355 dominant BVOC group throughout the season with an average of $6,600 \pm 6,700$ µg m^{-2} h^{-1} for the early season and $1,900 \pm 1,300$ 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).

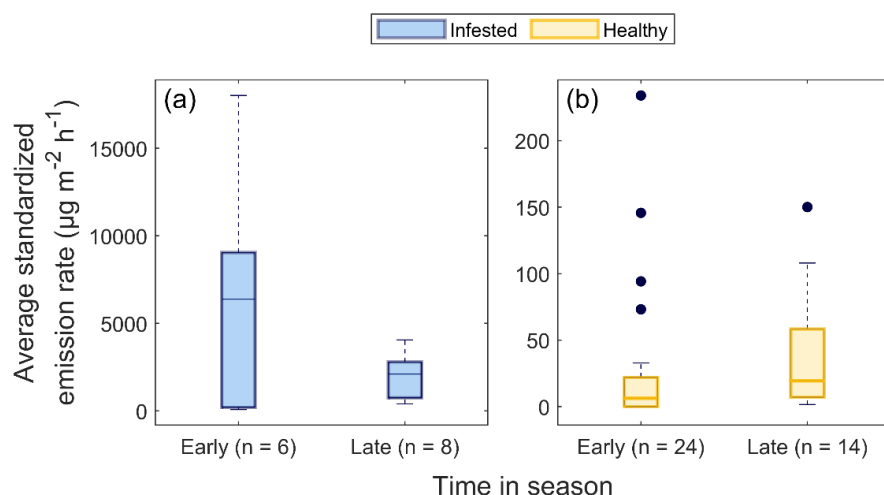
360 For all measured Norway spruce trees at both sites, a total of 74 individual BVOCs were found whereof 32 were MTs, 5 were SQTs and 37 were classified as other BVOCs including isoprene. For the healthy Norway spruce tree samples in HTM (n = 113), 44 individual compounds were found in total, where 12 were MTs, 2 were SQTs and 30 other BVOCs including isoprene. The infested Norway spruce trees measured at both sites had fewer samples (n = 38) compared to the healthy trees but a higher number of individual compounds was found with 52 compounds

365 in total. The majority of the compounds were MTs (n = 30, which was more than double the number compared to the healthy trees). There were also more SQTs (n = 5) found in the infested tree samples, but fewer 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

370 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 standardized bark BVOC emission rate when

375 comparing healthy and infested trees from all plots and sites for both seasons ($P<.001$; Fig. 6). 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 early and late seasons, respectively

(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).

380 **Figure 6: Boxplots of the temperature standardized emission rates of (a) the infested Norway spruce trees (blue) and (b) the healthy Norway spruce trees (yellow) during the early and late 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 daily averages are indicated by n and the black dots**
385 **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). The emission rates from infested trees during both seasons were significantly higher compared to the healthy trees (*P*<.001 for both), while there was no significant difference between the healthy trees during the early and late season (*P*>0.4).**

390 A difference in the occurrence of compounds was found between the healthy and infested trees at both sites (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 %). These MT compounds were also the most common in infested Norway spruce trees in both seasons, but were present in a higher proportion of samples (88-100 %) relative to the healthy trees. Infested trees in the late season also had 100 % occurrence of
395 (1S)-camphene while that compound only occurred in 75 % of the samples for infested trees in 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 with longifolene+β-caryophyllene occurring most (55 %) followed by α-humulene (18 %) which occurred in fewer
400 samples compared to the early season. The SQTs germacrene D, isoledene and β-cubebene were only emitted from one infested tree during the early season.

Isoprene was the most commonly occurring compound 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
405 %), benzene (45 %), nonanal (38 %) and toluene (21 %) were the most common compounds in 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 the most common compounds (after isoprene), however, for infested trees in the late season, 2-methyl-3-buten-2-ol was not emitted and 2-methyl-1-phenylpropene occurred in only 9 % of the samples.

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The emission rates for all compounds were higher in infested trees relative to healthy trees. The difference in emissions ranged from a 3-fold increase to a 2580-fold increase in infested compared to healthy trees in both

seasons (Table 3). The MT group had the highest (230-fold) increase during the early season compared to the 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 higher in infested trees) during the early season (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 rates (µg m^{-2} h^{-1} ± one standard deviation) from all Norway spruce trees located in Hyltemossa and Norunda. Presented are the frequently occurring 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 could not be quantified are presented as n.q. (no quantification). A full list of all identified compounds is found in the Appendix (Table A1).

Compound name	Healthy		Infested early season			Infested late season		
	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 emissions with number of bark beetle holes

The temperature standardized emission rates (TS) for all BVOC compounds combined from the bark beetle infested Norway spruce trees from both sites ranged from 170 to 13,500 $\mu g\,m^{-2}\,h^{-1}$ throughout the measurement period (Fig. 7). The daily average TS emission rate per bark beetle hole for infested trees during the early season was $22 \pm 29\ \mu g\ hole^{-1}\,h^{-1}$ and $4.4 \pm 3.5\ \mu g\ hole^{-1}\,h^{-1}$ for the late season. When scaling the TS emission rates with the average number of bark beetle holes (BBH), a comparison with the original TS emission rates showed that the average for all BVOCs combined BBH emission rates were higher (Fig. 7). During the early season the BBH emission rates were 2,500 $\mu g\,m^{-2}\,h^{-1}$ higher ($9,200 \pm 6,200\ \mu g\,m^{-2}\,h^{-1}$) compared to TS emission rates ($6,700 \pm 5,000\ \mu g\,m^{-2}\,h^{-1}$) and for the late season the BBH emission rates were 150 $\mu g\,m^{-2}\,h^{-1}$ higher ($900 \pm 650\ \mu g\,m^{-2}\,h^{-1}$) compared to the TS emission rates ($750 \pm 400\ \mu g\,m^{-2}\,h^{-1}$). For the individual trees, the BBH emission rates were higher compared to the TS emission rates for all infested trees but two (S1S1 and S5S3) which had higher TS emission rates of 270 and 95 $\mu g\,m^{-2}\,h^{-1}$, respectively compared to BBH emission rates (Fig. 7). The inconsistent variation in emission rate scaled with BBH or TS can be explained by the difference in the 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 average number of holes per square meter of bark. By applying a seasonal average derived from the results in Eq. 3, variations in emission rates caused by differences in the number of holes can be disregarded. The results from the infested trees are presented as BBH emission rates from here onwards unless stated otherwise.

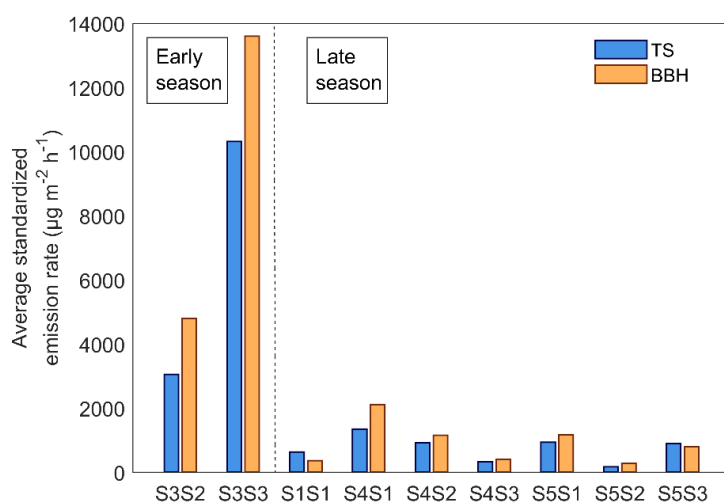



Figure 7: The seasonal average temperature standardized emission rate for all BVOCs combined from all infested Norway spruce trees located in Hyltemossa and Norunda. The tree ID is presented on the x-axis and is separated into early and late season (<100 or >100 days since infestation start, respectively). The temperature standardized emission rates (TS) are presented in blue, while the emission rates 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 how the emission changed with time after Norway spruce trees were infested by spruce bark beetles, measurements were taken at different intervals after the start of infestation at HTM and NOR. The earliest measurements occurred 12 days after infestation and showed an average emission rate for all BVOCs combined of 1,850 $\mu g\,m^{-2}\,h^{-1}$, 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 3,050-3,300 µg m^{-2} h^{-1} and 1,900-2,500 µg m^{-2} h^{-1} respectively (Fig. 8b,d). Eucalyptol was emitted at lower rates of 5 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 average of all BVOCs decreased with 80 % on average, with emissions ranging from 100-500 µg m^{-2} h^{-1}. The emission rates were still at higher levels than the seasonal emissions from healthy Norway spruce trees in HTM (30 µg m^{-2} h^{-1}; Fig. 8). Compared to the average emission rate of all BVOCs 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 (89 %). Eucalyptol did not have as distinct a decrease and had only decreased by 10 % 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 average of all BVOC emission rates from that tree were 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 70 and 270 µg m^{-2} h^{-1} respectively. However, after 350 days the emission rates went down to 32 and 58 µg m^{-2} h^{-1} respectively, also comparable with the emissions from healthy trees at that time (45 µg m^{-2} h^{-1}).

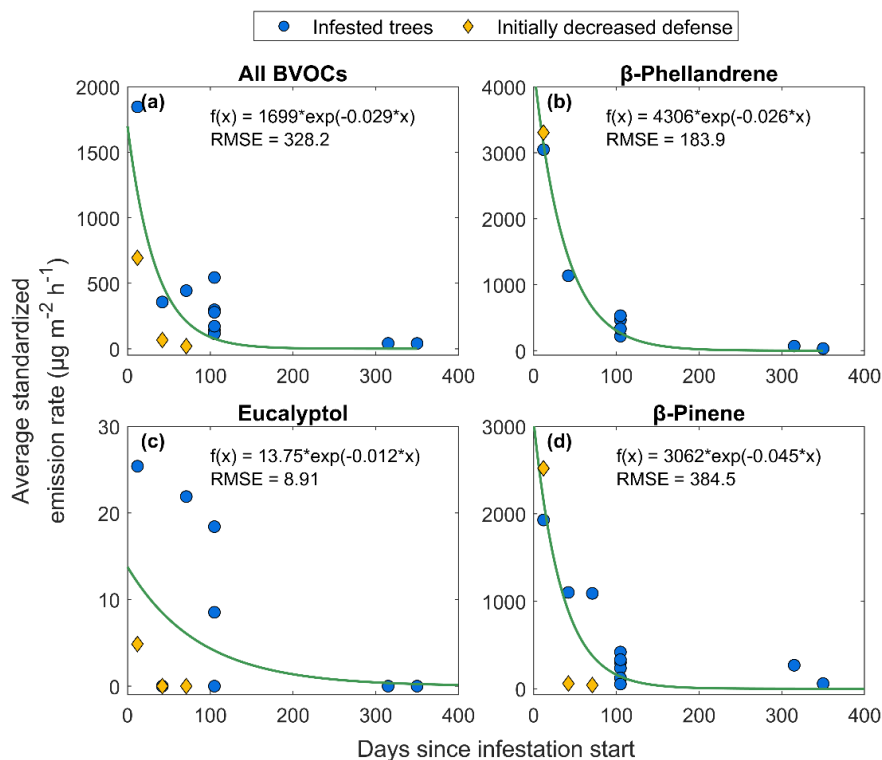



Figure 8: The relationship between average temperature standardized emission rate from all infested Norway spruce trees (blue circles) in Hyltemossa and Norunda and the number of days since infestation start for (a) the average of all BVOCs, (b) β-phellandrene, (c) eucalyptol and (d) β-pinene. An exponential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

 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 of hole (entry or exit) and time since infestation. The temperature standardized BVOC emission rates from all compounds 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

495 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

500 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).

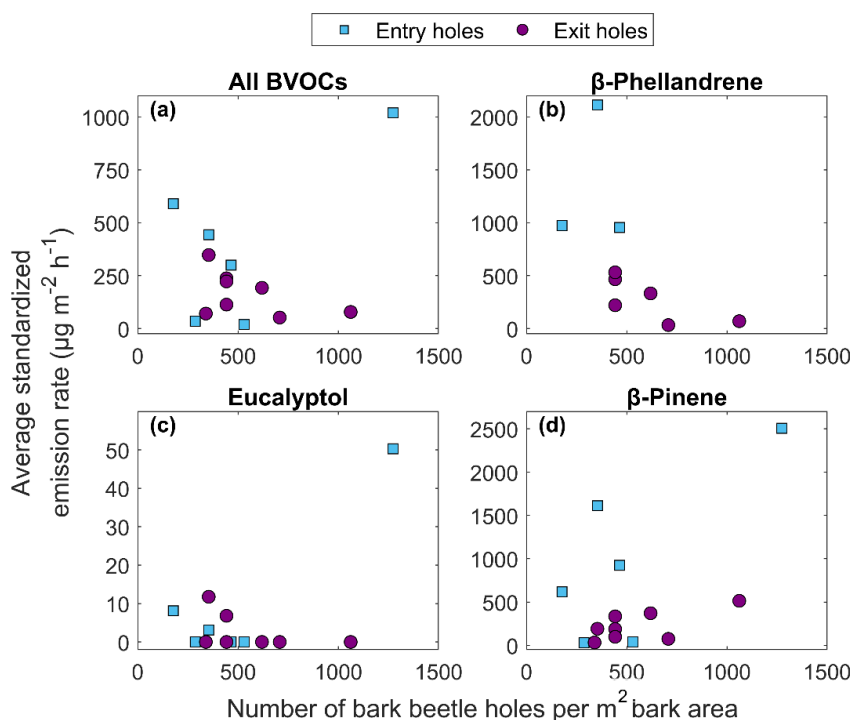



Figure 9: The relationship between average temperature standardized emission rate from infested Norway spruce trees in Hyltemossa and Norunda and the number of bark beetle holes per m² bark area for (a) the average of all BVOCs,
505 **(b) β-phellandrene, (c) eucalyptol and (d) β-pinene. The bark beetle 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

The result of the comparison between two individual trees is presented in this section. The different initial status of the trees can be identified in Fig. 10 (a,b) when measurements were taken in May before the infestation started.
510 The tree S3S2 had higher total emission rate of bark BVOCs compared to the healthy Norway spruce (S3S3) and the remaining two Norway spruce trees on plot 3 (healthy). The healthy trees only had four compounds identified in May, longifolene+β-caryophyllene, α-humulene and isoprene with low emission rates that remained at the same level throughout the measurement period (Fig. 10). When the bark beetle infestation started in June, the emission rates increased for both S3S3 and S3S2 but they showed differences in compound blend (Fig. 10c,d). The tree
515 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 June samples from S3S2 did however contain the bark beetle pheromones germacrene D, isoledene and β-cubebene which were not found in

the compound blend from S3S3 (Fig.10c,d). In July, the emission rates from S3S2 were lower 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 (Fig. 10g,h), but a new compound was identified from tree S3S3, verbenone, which could not be quantified in the study (Table 3).

The individual compound blend was also monitored qualitatively for tree S3S3 and indicated a change in the blend over time from healthy to infested (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 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 the 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 to 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).

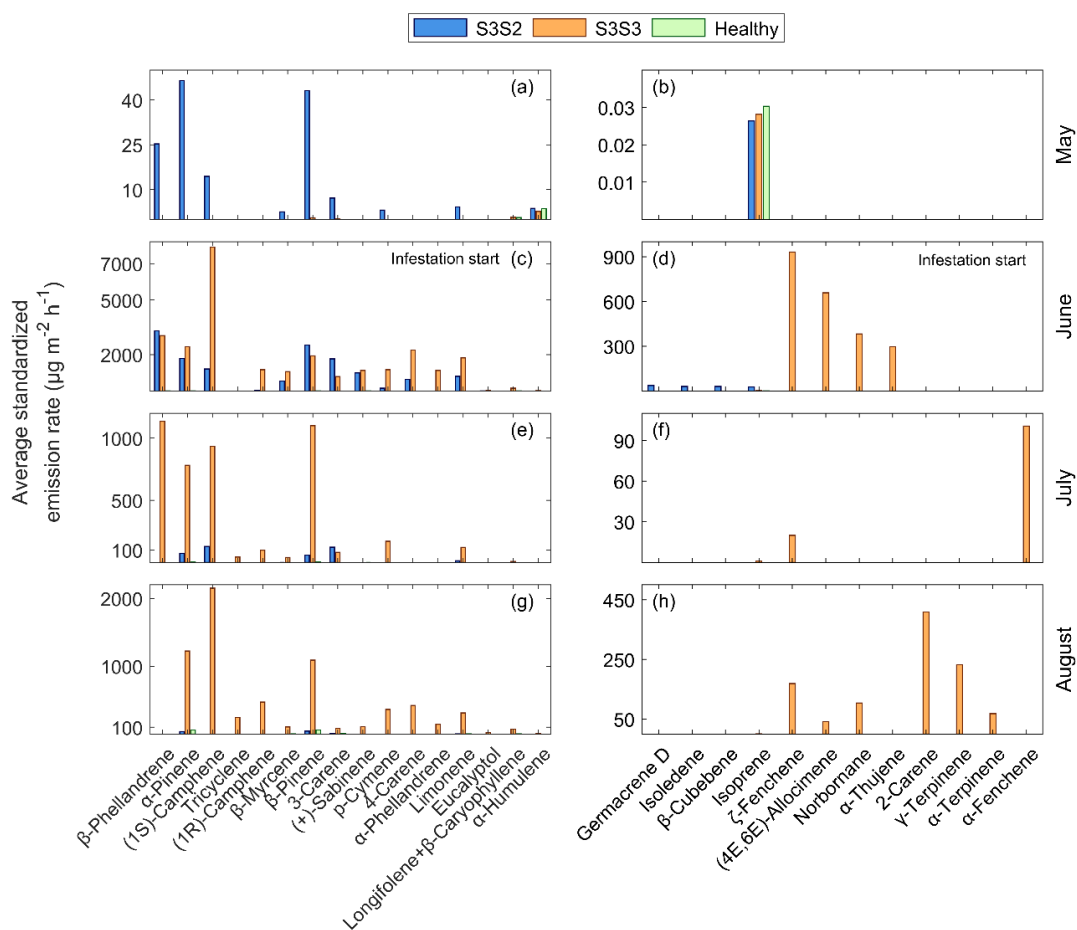



Figure 10: The daily average temperature standardized BVOC emission rates for all compounds from Norway spruce at plot 3 in Hyltemossa: infested spruce with ID S3S2 (blue), infested spruce with ID S3S3 (orange) and healthy trees (green). Measurements were taken in 2019 during (a,b) May, (c,d) June, (e,f) 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 results 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 compared to healthy 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 ranged 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 lower than 0.01-fold increase from healthy to infested and the Q_{10} coefficient for p-cymene actually had a 34 % reduction 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 5-fold increase 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 60 to 170 µg m^{-2} h^{-1} for needle MT in July and August and an average of 25 to 100 µg m^{-2} h^{-1} 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 (M_s), 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 of 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 healthy 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 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,

585 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,
590 bark emissions from infested trees were much higher (Fig. 11a). The measured bark MT emission rate from the infested tree reached up to 17,800 μg m^{-2} h^{-1}, 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 (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
595 and bark; Fig. 11). Bark MT emission rates from infested trees were at least 55 times higher than the total MT emission rate from both needles and bark of a healthy tree.

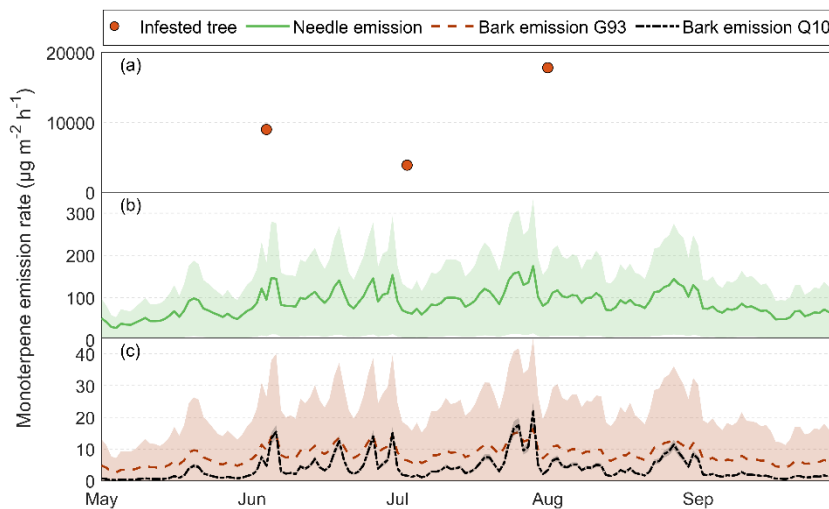
For the SQT emission rates, the difference was not as distinct. The SQT emission rate reached a maximum of 0.75 μg m^{-2} h^{-1} for bark emissions (Fig. A2b) and 30 μg m^{-2} h^{-1} for needle emission (Fig. A2a) while the measured bark
600 emission rate from the infested tree peaked at 40 μg m^{-2} h^{-1}, 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 1.4 μg m^{-2} h^{-1}, which was still higher than the calculated healthy bark emission rate at 0.2 μg m^{-2} h^{-1}, but lower than the needle emission rate of 5 μg m^{-2} h^{-1}.

605

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 needle emission rates were taken from van Meeningen et
610 **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 shades) represent the standard**
615 **deviation from the mean for the respective calculation method.**

4 Discussion

4.1 Bark BVOC emissions from healthy and infested Norway spruce

Both emission rates and compound composition of bark BVOCs from Norway spruce were found to change when trees were infested by spruce bark beetles, which is in line with previous studies on bark beetle infestation of conifers (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 were only emitted from infested trees which is 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 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 emissions uncertain. Ghimire et al. (2016) also assessed lichen coverage and isoprene emission and their results are consistent with this study: they did not find any statistically significant relationship between isoprene emission from bark and lichen or algal cover.

Bäck et al. (2012) previously showed that BVOC emissions between trees are likely to differ in their chemical composition, even between trees from the same forest stand. The Norway spruce trees measured in this study were from two different sites, HTM and NOR, which do not have genetically identical trees. However, the potential influence from genetics on the emission rates from Norway spruce trees between HTM and NOR sites were addressed in a study by van Meeningen et al. (2017) in which no significant differences were found for any compounds but isoprene. In this study, the majority of the compounds identified were MTs, and the main difference detected was between healthy and infested trees with similar results for both sites.

The results of this study indicate much greater increases in BVOC emission rates from healthy and infested conifer trees compared to previous findings (Amin et al., 2013; Ghimire et al., 2016; Heijari et al., 2011). In this study, the total BVOC emission rates for all compounds combined from infested Norway spruce bark were found to be 63- to 215-fold higher compared to healthy trees, in the early and late season respectively (Fig. 6). Previous findings reported increases in emission rates of up to 3-fold in Engelmann spruce (*Picea engelmannii*) infested by spruce beetles (*Dendtoctunus rufipennis*; Amin et al., 2013), up to 10-fold in Scots pine (*Pinus sylvestris*) infested by weevils (*Hylobius abietis*; Heijari et al., 2011) and up to 15-fold highr emission rates of total 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). As the emission rates in the study by Ghimire et al. (2016) were standardized according to G93, a temperature effect on emission rates cannot explain this large difference when comparing the increase in emission rates between healthy and infested Norway spruce trees with the results in this study. A possible reason might however be the time since infestation start in relation to when the measurements were conducted. The emission rates decreased exponentially with time after infestation (Fig. 8), suggesting that if sampling occurred 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 what Ghimire et al. (2016) found in June. Direct comparison with the emission rates reported by Ghimire et al. (2016) and our data is complicated by the lack of information of the time since infestation in their data, and it is possible that emissions observed in 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 show that emission rates from infested Norway spruce bark 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 after 30 days. However, 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). The long period of induced emission rates would suggest that the increased emission rates and their exponential decay over time were not only due to the exposure of resin which hardens over time, but also because of the active defense of the tree which decreased over time as the bark beetle infestation proceeds. The different hole types provide an indication of the bark beetle infestation development, where entry holes are found early during the infestation and exit holes later when the defense is lower. There was no distinct pattern when comparing the total number of holes to emission rates for the individual Norway spruce trees (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, supporting the claim that the exponential decay is not only due to hardening resin since the difference in emission rates from the hole types would not be as apparent in that case (Fig. 9). This is also 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), and the same is true for the compounds β-phellandrene, eucalyptol and β-pinene (Fig. 9). This result supports the conclusion that emission rates are linked to the time since infestation start, which might be explained by the tree defense being most active in the beginning of an attack and declining over time.

The number of identified BVOC compounds emitted from entry holes were higher compared to exit holes (Table 3), which further supports the assumption that the emission rates are due to the ecological impacts of the spruce bark beetles and not only due to exposed resin. This is consistent with Birgersson and Bergström (1989) who looked at volatiles emitted from entry holes in bark beetle infested Norway spruce. Although they did not look at exit holes, 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 emitted from entry holes in this study – however, only from one tree (tree ID S3S2) and only during measurements in June (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. Although they did not measure the emission rates from the bark as done in this study, 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

As two trees with different health status were infested by bark beetle at plot 3 in HTM, we were able to conduct a small case study with measurements of the BVOC emissions throughout an infestation, both from a fully healthy (ID S3S3) tree and from a tree attacked by bark beetles the preceding season (ID S3S2). The initial results of this case study indicate differences in emission rates and compound blend from trees with different health status. However, as these results are based on a small sample size they should be followed up in future studies.

Prior to the infestation, we found that the emission rate of the healthy tree (ID S3S3) was lower compared to the seemingly stressed tree (ID S3S2; Fig. 10a,b). High emission rates may indicate stress supporting the claim that tree S3S2 was already stressed (Loreto and Schnitzler, 2010). This was also visible from old resin flow on the bark indicating that the high emission rates were caused by a late summer attack from spruce bark beetles from the previous year. As both trees were infested in June, their emission rates increased but they had a slightly different compound blend which might have been caused by their initial health status. Bark beetle pheromones were found in the June samples from tree S3S2, something that could indicate that there was ongoing blue stain fungi infection caused from the old infestation or that the new bark beetles had already established in the tree again (Birgersson et al., 1988; Zhao et al., 2011a). Over time, the emission rates decreased for tree S3S2 while they remained at higher levels for tree S3S3 which could be an indication of the lower vitality of spruce S3S2 and the higher resistance from the initially healthy spruce S3S3. The defense from spruce S3S3 seemed to be ongoing up until the trees were cut down in August, however, the last measurement in August did reveal the occurrence of verbenone, a compound that is emitted after successful fungal establishment and repels bark beetles (Bakke, 2009; Cale et al., 2019). This could indicate that the bark beetles had successfully overtaken the Norway spruce S3S3 in August, however this could not be confirmed because the trees were cut down, preventing us from taking further measurements.

As bark beetle outbreaks increase, 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). This further highlights the need for follow up studies on the initial results of our case study, because healthy trees might contribute to higher emission rates upon infestation compared to already weakened trees. The results from this study revealed different blends of compounds when a tree was already stressed from a previous infestation and attacked again compared to when the tree was healthy before the attack. Another important note from the case study is that emission rates after bark beetle infestation can remain high for up to a year but still be further increased after a new infestation. This is evident from the previously attacked tree (S3S2) which had induced emission rates until the start of the next season (measurements in May Fig. 10a,b), during which the tree was infested again with further induced emissions. These results indicate that the second generation of spruce bark beetles, normally attacking late during the growing season, might lead to induced emission rates continuing until the next year. The initiation of a second generation of spruce bark beetles might thus have a larger impact compared to only attacks from one generation on the total bark BVOC emission rates from Norway spruce because the emission rates are then induced for longer.

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

High BVOC emission rates from infested trees do not only affect the trees themselves, but also impact atmospheric processes. Induced emission rates of BVOCs due to insect herbivory can potentially increase SOA yields in a

745 modelling study (Bergström et al., 2014). 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 the 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 compared to healthy trees (Table 3). The MTs limonene and myrcene were slightly below the SQTs in

750 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. Therefore, the observed changes in BVOC compound composition due to bark beetle infestation found in this study could potentially lead to large impacts on SOA yield and highlights the importance of measuring and accounting for bark BVOC emissions.

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An increase of attacks on healthy trees might further affect the atmospheric processes, specifically production of SOA. In the case study with the initially stressed tree (S3S2) and the initially healthy tree (S3S3), both trees had similar emission rates, but they emitted different compound compositions. Higher emissions of limonene and myrcene were measured from S3S3 early during the infestation which might indicate that increased attacks on

760 healthy trees can affect the production of SOA more than attacks on already weakened trees. The high emission rates also continued until the trees were cut down in August, implying that potential increases in SOA yield might continue for longer compared to emissions from already weakened trees.

Significant increases of the temperature standardized BVOC emissions of Norway spruce bark were seen when

765 trees were infested by bark beetles early in the season. Around a 230-fold increase in emission rate was seen for the MTs group. This high increase in emission rate from insect stress for Norway spruce has not previously been observed according to a review by Yu et al. (2021), in which the highest recorded increase was around 20-fold, 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

770 temperatures of 40 °C found that BVOCs increased 1.8-fold compared to emission rates at air temperature of 30°C (Esposito et al., 2016). This is 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

775 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. Taking this into account, and the fact that bark beetle infestations

780 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 combined stress when modelling the emissions and to include it in follow up studies.

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 during the 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 time during 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, and if the outbreaks are sustained at high levels, there would be large impacts regionally. During 2020 in Sweden, 8 million m³ 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 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). As evidenced 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 emit BVOCs from their bark as a stress response to spruce bark beetles, and as the number of spruce bark beetle outbreaks is expected to increase in a warmer climate, it will impact the total emission of BVOCs. The aim of this 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, how emission rates develop

825 over time after infestation and to analyze the difference in emissions from different bark beetle drilled holes. During the study, an opportunity arose allowing us to investigate how the BVOC emissions change from non-infested to infested and throughout the infestation.

  The results show that there is a significant difference in BVOC emission rates from healthy and infested Norway
830 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 a tree was infested a second time the following season, the already increased emission rates
835 were further increased to reach the same levels as induced emissions from a tree infested for the first time. As the infestation proceeded, there was a difference in the emission rate and compound composition 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.

840 Further studies are needed to support the findings from this study on the change in emission rates and compound composition when healthy trees are infested compared to weakened trees as well as the potential increased impact from combined stresses. There is also a need for further studies to analyze the entire impact of spruce bark beetles over long periods and from all parts of 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
845 and could potentially lead to a 1.1-fold increase of total MT emissions from Norway spruce in Sweden. 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
850 trees and more frequently throughout the season are needed in order to fully understand their 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).

Compound name	Healthy		Infested early season			Infested late season		
	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	

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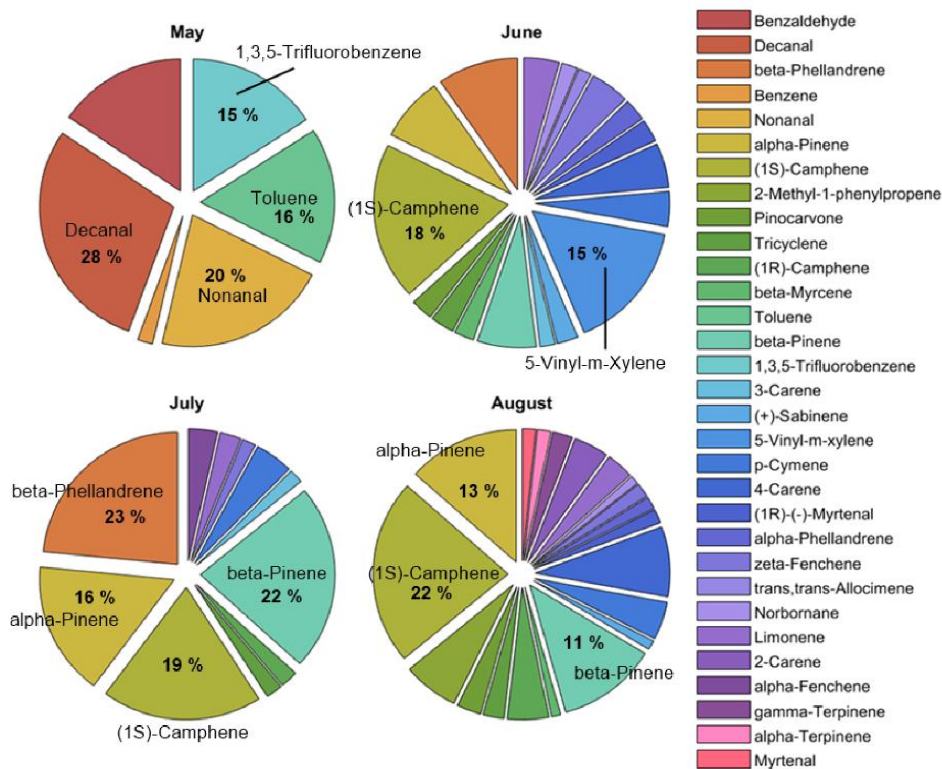
Figure A1: The daily average blend from the Norway spruce S3S3 and percentage contribution in mass throughout the summer (May, June, July and August), showing only compounds with a mass contribution of at least 1 %.

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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
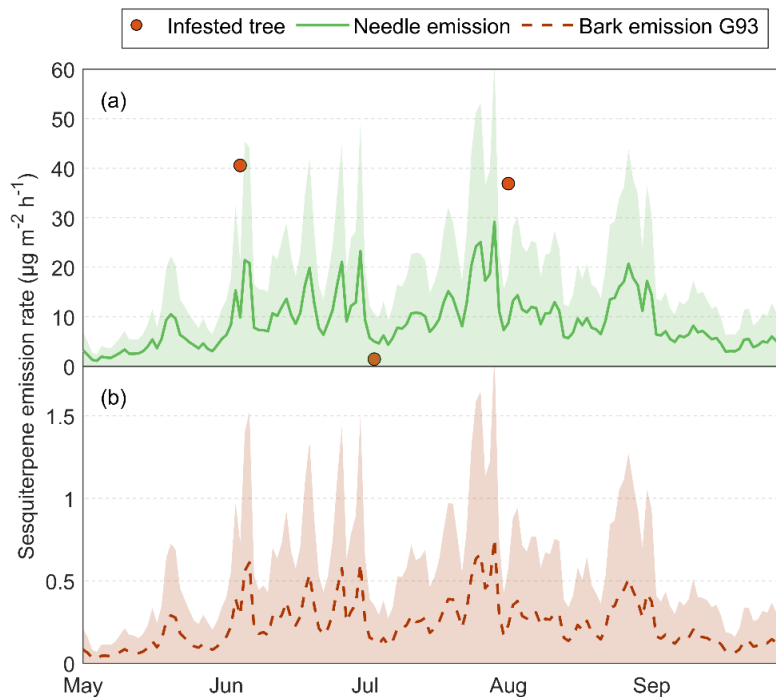
Figure A2. The measured and calculated BVOC emission rates for the group sesquiterpenes from Norway spruce in Hyltemossa: (a) the actual measured emission rates from infested Norway spruce bark (red dot) and calculated needle emission rates (green line) and (b) calculated healthy bark emission. The needle 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.

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