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Effect of bark beetle (*Ips typographus* L.) attack on bark VOC emissions of Norway spruce (*Picea abies* Karst.) trees

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HIGHLIGHTS

- Beetle attack increases the emissions of MTs but decreases those of several SQTs.
- α-Pinene, camphene and myrcene are the most responsive bark beetle induced MTs.
- α-Pinene emission has positive correlation with mean trap catch of bark beetles.

GRAPHICAL ABSTRACT

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ABSTRACT

Climate warming driven storms are evident causes for an outbreak of the European spruce bark beetle (*Ips typographus* L.) resulting in the serious destruction of mature Norway spruce (*Picea abies* Karst.) forests in northern Europe. Conifer species are major sources of biogenic volatile organic compounds (BVOCs) in the boreal zone. Climate relevant BVOC emissions are expected to increase when conifer trees defend against bark beetle attack by monoterpene (MT)-rich resin flow. In this study, BVOC emission rates from the bark surface of beetle-attacked and non-attacked spruce trees were measured from two outbreak areas, Iitti and Lahti in southern Finland, and from one control site at Kuopio in central Finland. Beetle attack increased emissions of total MTs 20-fold at Iitti compared to Kuopio, but decreased the emissions of several sesquiterpenes (SQTs) at Iitti. At the Lahti site, the emission rate of α-pinene was positively correlated with mean trap catch of bark beetles. The responsive individual MTs were tricyclene, α-pinene, camphene, myrcene, limonene, 1,8-cineole and bornyl acetate in both of the outbreak areas. Our results suggest that bark beetle outbreaks affect local BVOC emissions from conifer forests dominated by Norway spruce. Therefore, the impacts of insect outbreaks are worth of consideration to global BVOC emission models.

1. Introduction

Biogenic volatile organic compounds (BVOCs) refer to organic atmospheric trace gases and non-methane hydrocarbons that are emitted by plants or other organisms (Laothawornkitkul et al., 2009). The BVOCs comprise four main compound categories: isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), other reactive VOCs and other less reactive VOCs (Laothawornkitkul et al., 2009). Globally, BVOCs with an amount of 1150 Tg (C) y^{-1} constitute more than 50% of all atmospheric VOCs (Guenther et al., 1995; Hallquist et al.,

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2009). The BVOC emissions from plants increase with abiotic stresses (e.g. high temperature, high solar radiation) alone or together with insect herbivore and pathogen attacks. The BVOCs function in communication with other plants and organisms (Peñuelas and Llusia, 2003; Heil and Karban, 2010; Holopainen and Gershenzon, 2010; Loreto and Schnitzler, 2010), and play a role in plant growth, development, reproduction, and defense (Peñuelas and Llusia, 2003; Loreto and Schnitzler, 2010).

The BVOCs from natural vegetation may significantly alter the chemistry of the lower atmosphere. Photochemical reactions of BVOCs and nitrogen oxides (NOx) result in the formation of ozone (O_3) (Pinto et al., 2010). The BVOCs react with hydroxyl (OH) and nitrate (NO_3) radicals and O_3 in the troposphere (Atkinson and Arey, 2003), and they form a large amount of extremely low-volatility vapors and result in the formation of secondary organic aerosols (SOA) on condensation (Virtanen et al., 2010; Ehn et al., 2014). The BVOCs contribute up to 90% to SOA formation (90 Tg (C) y^{-1}) (Kanakidou et al., 2005; Hallquist et al., 2009). Bergström et al. (2014) estimated that the biotic stress-induced BVOC emissions from European forest ecosystems occasionally contribute more to SOA production than the constitutive emissions. Resin-storing conifers are important emission sources of reactive monoterpenes (Ghimire et al., 2013). Laboratory chamber experiments showed that feeding by pine weevils (*Hylobius abietis* L.) increased VOC emissions from Scots pine and Norway spruce seedlings by 10–50 fold resulting in 200–1000 fold increases in SOA masses formed via ozonolysis by added ozone (Joutsensaari et al., 2015). In a modelling study, Berg et al. (2013) reported that BVOCs induced by mountain pine beetle (*Dendroctonus ponderosae* Hopkins) from lodgepole pine (*Pinus contorta var. Latifolia* Engelm.) and other bark beetle (species not identified) from Engelmann spruce (*Picea engelmannii* Parry ex Engelm.) trees may lead up to a 3-fold increase in atmospheric SOA. Aerosols affect the radiative balance of Earth's atmosphere by scattering and absorbing solar and terrestrial radiation (Boucher et al., 2013). Significant aerosol nucleation events have been detected in the boreal environment also in winter and spring (Kulmala et al., 1998), when BVOCs participate actively in atmospheric processes. However, a global chemical transport model suggests that the summertime source of Aitken mode (30–110 nm) and nucleation mode (110–700 nm) aerosols may contribute more to cloud condensation nuclei than the accumulation mode aerosols (110–700 nm) in spring season (Korhonen et al., 2008).

European boreal forests, dominated by conifers, are characterized by large BVOC emissions. The average total BVOC emission in two years (2004 and 2005) obtained from Pan-European domain is 12 Tg (C) y^{-1} with forest contributing 55% to this emission (Karl et al., 2009). Norway spruce (*Picea abies* Karst.), the second most dominant tree species, covers 30% of the total growing stock (2206 million m^3) in Finland (Peltola, 2009). Norway spruce synthesizes oleoresin, a mixture of diterpenes (C_{20}) and monoterpenes (MTs) for protection against insect herbivores and other organisms (Steinbrecher et al., 1997). Monoterpenes dominate BVOC emissions from non-isoprene emitting coniferous trees (Geron et al., 2000), and contribute 10% to global MT emissions (Guenther et al., 1995), while the emission of sesquiterpenes (SQTs) is relatively low. Conifer trunks are attacked by a wide range of organisms including insects, vertebrates, fungi and bacteria as phloem under the bark is rich in organic nutrients (Franceschi et al., 2005). Conifer trees defend against attacks by bark beetles by resin flow which mostly releases MTs into the atmosphere during polymerization resulting in the formation of protective solid plug (Eller et al., 2013). For example, lodgepole pine trees attacked by *D. ponderosae* are known to increase bark emissions of MT up to 4-fold (Berg et al., 2013) and total BVOC emissions by a 5-to 20-fold (Amin et al., 2012). Engelmann spruce trees attacked by bark beetles increase bark emissions of MT by 3-fold (Berg et al., 2013) and total BVOC emissions by 9-fold (Amin et al., 2013). Likewise, *H. abietis*-damage to young Norway spruce bark increased systemic needle BVOC emissions 5-fold and doubled bark emissions (Blande et al., 2009), while the weevil damage on Scots pine (*Pinus sylvestris* L.) seedlings triggered 4-to 7-fold increase in bark emissions and nearly 3-fold increase in needle BVOC emissions (Heijari et al., 2011).

Climate warming promotes early swarming and multi-voltinism of bark beetles by reducing the length of overwintering period in soil (Jönsson et al., 2009). Climate extremes such as increased intensity of storms and periods with low precipitation result to stressed, weakened, and recently wind-thrown trees which are good reproduction sites for bark beetles (Gitau et al., 2013). For example, disastrous storms in 1990s and 2000s resulted in extensive outbreaks of European spruce bark beetle (*I. typographus* L. Coleoptera: Curculionidae) in central and northern Europe (Wermelinger, 2004; Komonen et al., 2010). The mean mortality rate of Norway spruce typically peaks in the second or third summer following the storm disturbance due to bark beetle dispersal to uninfested stands (Schroeder and Lindelöw, 2002). *Ips typographus* outbreaks with two generations annually occur in southern and south-eastern parts of Finland since the exceptionally warm summer and summer storms in 2010 (P. Lyytikäinen-Saarenmaa, personal observation).

Ips typographus is an aggressive beetle species and the most severe pest of Norway spruce throughout Europe. The attack rates have been found to respond positively to increased summer temperature (Chinellato et al., 2014). Early symptoms of attacks by adult bark beetles are entrance holes (approximately 2–3 mm in diameter), resin flow and brownish frass in spruce bark crevices and trunks. Larval feeding in the bark and phloem leads to disrupted moisture balance in trees, followed by yellowish and then reddish-brown foliage. Larvae feed under thick bark of weakened or dying spruce trees, but adults can attack healthy hosts during the peak phase of an outbreak. Depending on the latitude, numerous round exit holes by the first generation young adults appear from late June to August (Öhrn et al., 2014).

Since mature Norway spruce forests are under the threat of expanding bark beetle attacks, we selected two Norway spruce forest sites (Iitti and Lahti) attacked by *I. typographus* and one unattacked forest site at Kuopio as control for the assessment of *I. typographus* outbreak effects on bark BVOC emissions. Our goal was to determine if (1) attack and feeding damage by bark beetles in the authentic attack site increases the emission rates of BVOCs from Norway spruce bark and if (2) the emission rate is correlated with mean beetle attack density or mean trap catch on study plots, since these are often used as indicators of bark beetle attack intensity. Some soil growing and epiphytic lichen species can be the sources and sinks of volatile and semi-volatile organic compounds (Kesselmeier et al., 1999; Schrlau et al., 2011). Epiphytic lichens (mainly *Hypogymnia physodes* L., Nyl.) and algal cover are commonly found on the bark surfaces of most spruce trees. Therefore, we also wanted to know if lichen and algal cover of the VOC sampling area contributes to BVOC emission rates from the bark surfaces. This study will help to estimate the impacts of bark beetle outbreak on the atmospheric BVOC budget in the disturbed areas.

2. Materials and methods

2.1. Study sites

A Norway spruce stand attacked by *I. typographus* was located at Haapa-Kimola of Iitti municipality (site 1) in southern Finland

(60°53′ N, 26°20′ E, 69 m above sea level (asl)). The *I. typographus*-free study site (site 2) was at Ruohoniemi in the city of Kuopio (62°37′N, 26°11′E, 80 m asl). The third study area (site 3) covered eight urban forest stands infested with bark beetles and was located at Lahti city (60°59′ N, 25°39′ E, 105 m asl) in southern Finland.

2.2. VOC sample collection

2.2.1. Iitti and Kuopio (2011)

VOCs were collected at the Iitti site on 29 June 2011 for the first time. Twelve Norway spruce trees attacked by bark beetles (coded as BAT_{Iitti} = beetle attacked trees of Iitti) were randomly selected in the vicinity of a conserved mature forest site, where restoration actions were carried out in 2008 by girdling Norway spruce trees. This gradual tree mortality caused increased population density of *I. typographus*. Four non-attacked trees were selected from a non-conserved forest stand close to the conserved forest area (at a distance of 500 m from the attacked trees) for the control group (coded as CT_{Iitti} = control trees of Iitti). All the trees coded as BAT_{Iitti} were sampled a second time on 16 August. Most of the control trees of Iitti sampled in June showed some physical symptoms of beetle damage (e.g. exit holes and resin flow on bark surfaces) in August. In order to obtain appropriate control trees, four healthy spruce trees were sampled at Kuopio site (coded as CT_{Kuopio} = control trees of Kuopio) on 22 August. The condition of the canopy (defoliation, discoloration), entrance holes of beetles and resin flow on tree bark surface were monitored. Mean diameter at 1.3 m ($D_{1.3}$) and height (h) of BAT_{Iitti}, CT_{Iitti} and CT_{Kuopio} trees were $D_{1.3}$ = 21.6 cm and h = 11 m, $D_{1.3}$ = 19.1 cm and h = 10 m, and $D_{1.3}$ = 15.8 cm and h = 10 m, respectively.

The VOCs were collected from the circular bark surface area of 167 cm^2 (usually free of resin drops and lines) using cleaned (120 °C for 1 h) disposable polyethylene terephthalate (PET) (size 25 × 38 cm, FREETIME, Suomen Kerta Oy, Finland) enclosure. The PET bag was fixed around silicon O-tubes and tightened with belts around the tree trunk at a height of 1.3 m. Clean charcoal-filtered and MnO_2 scrubbed air was pumped through Teflon tubing into the bags at a flow rate of 0.6 L/min to fill and replace air in the bags. The headspace sample was pulled through steel tubes filled with Tenax-TA and Carbopack-B adsorbents (1:1, 100/100 mg, mesh 60/80, Supelco, Bellafonte, PA, USA) with a vacuum pump (Rietschle Thomas 5002 12 V DC, Puchheim, Germany) at a rate of 0.2 L/min through an opening cut at the corner of the bag. The airflow was calibrated with the mini-Buck calibrator (Model M−5, A.P. Buck, Inc., Orlando, FL, U.S.A.). Volumes of VOC samples collected from the headspace of tree bark surfaces were 3L and 4L in June and August, respectively. The mean temperatures and photosynthetically active radiation (PAR) inside the collection bags were monitored with a HOBO Micro Station Data Logger, Onset Computer Corporation, Cape Cod, Massachusetts, USA during VOC samplings. The mean value of temperatures were 24 °C (June) and 20 °C (August) at Iitti site, and 18 °C (August) at Kuopio site. The PAR levels monitored at a height of 1.3 m of tree trunk were below 100 μmol m^{-2} s^{-1} during each sampling in both locations of dense and shady spruce forests. Blank samples were also collected using empty collection bags to detect impurities originating from the collection system. The concentrations of the impurities were subtracted from the total emissions in order to quantify the real bark emissions.

2.2.2. Lahti (2012)

We collected VOCs from the bark surfaces of two-to-four randomly selected spruce trees in each of the eight urban forest stands at Lahti following the procedure described above. All of the eight forest stands were bark beetle attacked sites, where data on mean density of beetle entrance holes in trap logs and mean beetle number from pheromone traps (Ecotrap, baited with Ecolure lures, Phytofarm Inc., Slovakia) were available (Table 1). The mean temperatures inside the collection bags were 15 °C and 22 °C on 20 June and 15 August samplings, respectively. The PAR levels monitored from shady spruce trunks were below 100 μmol m^{-2} s^{-1} during both samplings. The sampled bark surface areas devoid of fresh or dry resin were photographed, and coverage of the epiphytic lichen *H. physodes* and algal growth therein were estimated visually from digital photographs. Presence of fresh resin flow at tree level was determined by visual observations in the field, and the trees were divided into healthy-looking without resin flow (coded as CT = control trees) and beetle-attacked with resin flow (coded as BAT = beetle attacked trees) groups.

2.3. VOC analyses

The VOC samples were analyzed by gas chromatography-mass spectrometry (GC–MS) (Hewlett Packard GC type 6890, MSD 5973, Beaconsfield, UK). Trapped volatile compounds were desorbed with a thermal desorption unit (Perkin–Elmer ATD400 Automatic Thermal Desorption system) at 250 °C for 10 min. The compounds were cryofocused at −30 °C, and transferred onto a HP-5 capillary column (50 m × 0.2 mm i. d. × 0.5 μm film thickness, Hewlett–Packard) with helium as a carrier gas. The temperature programme was 50 °C for 1 min, followed by increases of 5 °C min^{-1} to 210 °C and 20 °C min^{-1} to 250 °C. All mass numbers between 30 and 350 *m/z* were recorded using SCAN technique. Different VOCs were identified by comparing their mass spectra with the Wiley library and twenty-eight pure standards. The compounds not included in the standards were quantified by using reference compounds. The reference α-pinene was used for non-oxygenated MTs, 1,8-cineole for oxygenated MTs and longifolene for SQTs. The β-phellandrene was quantified by α-pinene; pinocarvone and myrtenal by 1,8-cineole; α-cubebene, longipinene, α-ylangene, longicyclene, β-bourbonene, isoledene, β-selinene, (*E*)-α-farnesene, germacrene-D, α-cedrene, γ-cadinene and five unidentified SQTs by longifolene. The peaks of β-pinene and myrcene as well as limonene and β-phellandrene were coeluted in the chromatography due to their higher emissions in some of the Iitti samples. Therefore, they have been presented together as a sum of two compounds in the Tables 2 and 3. The detection limit set in the chromatograms was 1 ng.

In order to make the emissions at different temperatures more comparable, terpene emissions were standardized to 20 °C, a suitable temperature for boreal environment (Ekberg et al., 2011) using the classic algorithm established by Guenther et al. (1993). We used the temperature coefficient (β) of 0.09 for MTs (Guenther et al., 1993) and of 0.16 for SQTs (Helmig et al., 2006) to standardize the emissions. Isoprene emissions were standardized at a temperature of 20 °C and PAR level of 1000 μmol m^{-2} s^{-1} using the model developed by Guenther (1997).

VOC emissions were calculated in μg $h^{-1}m^{-2}$ of bark area using the following equation:

$$E = (F(C2 - C1))/A$$

Where E = VOC emission, F = Flow rate of input air (l/h), C2 = concentration of compound per litre volume of output air (μg/l), C1 = concentration of compound in filtered input air (considered as 0 μg/l) and A = bark surface area (m^2)

Table 1
Geographic coordinates, bark beetle and tree stand characteristics of the eight urban-forest stands with study plots at Lahti outbreak area.[a]

Study plot Code	Geographic coordinates		Mean tree diameter (cm) (at 1.3 m)	Mean tree height (m)	Defoliation category (%)	Entrance holes in logs (m^{-2})	Mean trap catch	
	East, X	North, Y				(18–20 June)	June	August
5	3423781.53	6764775.52	40	31	25–49%	91	1150	714
7	3427263.63	6767661.21	37	26	25–49%	96	678	362
8	3433798.68	6766248.76	38	31	<25%	28	2807	1888
13	3429259.39	6766570.78	45	31	25–49%	49	2037	1525
20	3432238.00	6763819.00	NDA	NDA	NDA	41	NDA	NDA
25	3429473.43	6765364.85	49	32	<25%	58	1680	371
31	3433798.68	6766248.76	38	31	<25%	28	2807	1888
33	3426181.34	6765189.75	39	28	25–49%	43	974	732

[a] BVOC samples were collected from the bark surface of randomly selected Norway spruce trees of the pheromone trapped forest sites at Lahti. Entrance holes were calculated from trap logs and mean catch of *Ips typographus* from pheromone traps. Mean trap catch in June and August represent population density of *I. typographus* calculated separately from the weekly trap catch (mean of 3–5 traps) of 21 May–21 June and 2 July–15 August, respectively. NDA = no data available.

2.4. Statistical analyses

We tested the normality of the VOC emission data using the Kolmogorov–Smirnov test. In cases of non-normality, the data was logarithm (log 10(x + 1)) transformed or square root transformed to follow a normal distribution. The tree groups (CT_{Iitti} vs BAT_{Iitti} in June 2011, CT_{Kuopio} vs BAT_{Iitti} in August 2011, and CT_{Lahti} vs BAT_{Lahti} in June and August 2012) were compared using Independent Samples T-Test. In cases where the transformation did not normalize the data, Mann–Whitney U Tests were used. The relationship of VOC emissions of each forest stand with the corresponding mean trap catch, mean density of beetle entrance holes in trap logs and lichen-and algal cover was tested by Spearman's correlation analysis. The statistical analyses were conducted using IBM SPSS Statistics 19 for Windows (SPSS Inc, Chicago, IL, USA).

3. Results

3.1. BVOC emissions from bark beetle-attacked and non-attacked Norway spruce trees

At the Iitti site, bark beetle attacks did not influence the emission of total MTs (Fig. 1) in June. However, the emissions of terpinen-4-ol and α-terpineol were significantly decreased in the beetle attacked trees (Table 2). Beetle attacks significantly decreased the emissions of longipinene (by 55%), β-bourbonene (by 96%), and two unidentified SQTs in June (Table 2), although the emissions of total SQTs were unaffected (Fig. 1). The α-humulene, germacrene-D, γ-cadinene and an unidentified SQT present in non-attacked trees were absent in beetle attacked trees (Table 2). On the other hand, (*E*,*E*)-α-farnesene was present only in the beetle-attacked trees. The emission ratio of total MTs to total SQTs is significant (*P*-value = 0.004) with the mean (±SE) ratio of 458 ± 90 in the beetle-attacked trees against the ratio of 129 ± 17 in the control trees in June.

In August, emission rates of total MTs were significant and 20 times higher in beetle-attacked trees of Iitti compared to bark-beetle free trees at Kuopio (Fig. 1). The emission rates of α-pinene, camphene, limonene, and bornyl acetate were respectively 39, 55, 15 and 5-fold higher in the beetle attacked trees of Iitti than the control trees of Kuopio (Table 3). However, bark beetle attack had no significant effects on the emissions of total SQTs (Fig. 1). A monoterpene 1,8-cineole and a SQT, isoledene emitted by beetle-attacked trees were not found in the control trees of Kuopio. Bark beetle attack significantly increased the emission of nonanal by 2-fold at Iitti site compared to Kuopio (Table 3).

At Lahti site, beetle attacked trees emitted β-phellandrene that was not emitted by the control trees in June (Table 4). In August, the beetle attacked trees had higher emission rates of tricyclene (5-fold), camphene (3-fold), myrcene (21-fold) and 1,8-cineole (4-fold) compared to the control trees (Table 5). Camphor and α -terpineol emitted by the attacked trees were not present in the control trees. The emission of isoprene was detected in August (Table 5) from 38% of the total sampled trees. The increase in the emission rates of total MTs in the beetle attacked trees was not significant in June and August (Fig. 2).

The emission rate of α-pinene was positively correlated with mean trap catch (r_s = 0.775, *P*-value = 0.041, n = 7) in June. We observed a similar, but marginally significant correlation (r_s = 0.739, *P*-value = 0.058, n = 7) between β-pinene emission and the mean trap catch. There was no significant correlation between the emissions of volatile compounds from spruce trunks and the mean density of *I. typographus* entrance holes in trap logs (data not shown).

3.2. Effects of lichen and algal cover on bark BVOC emissions

At Lahti, the volatile compounds with positive correlation to lichen cover on bark surfaces were limonene (r_s = 0.467, *P*-value = 0.038, n = 20) and 1,8 cineole (r_s = 0.483, *P*-value = 0.031, n = 20) in June. Algal cover on the spruce bark surfaces was not correlated with the bark BVOC emissions in any of the sampling time (data not shown).

4. Discussion

Our results from Iitti site showed a distinct reduction in the emission rates of several sesquiterpenes (SQTs), but indicated a substantial increase in the emission ratio of total monoterpenes (MTs) to total SQTs from the bark surfaces of beetle-attacked trees in June. The changed emission ratio may indicate higher de novo MT biosynthesis that has inhibited carbon allocation for the biosynthesis of SQTs in the beetle-attacked trees. Correspondingly, simulated biotic stresses on the bark tissue of Norway spruce stem by methyl jasmonate (MeJA) elicitor induced a twelve-fold increase in MT emissions (Martin et al., 2002). A 20-fold increase of total MT emissions in August samples of Iitti compared to Kuopio site is at the same level as the emission rates of total BVOCs from the bark beetle-damaged trunks of *P. contorta* trees (Amin et al., 2012), but it is higher than the 9-fold increase of total BVOCs from the beetle-damaged trunks of *Picea engelmannii* (Amin et al., 2013). This induced emission rates of total MTs at Iitti compared to Kuopio site is 10 times higher than the 2-fold increase of total MT emissions from Norway spruce bark inoculated with *Ceratocystis polonica*, *a*

Table 2
Mean (±SE) VOC emissions from bark surfaces of Norway spruce trees at Iitti site in June 2011.[a]

Emission (μg h^{-1} m^{-2} (bark area))	CT_{Iitti}	BAT_{Iitti}	P-value
Monoterpenes			
Tricyclene	0.9 ± 0.5	1.5 ± 0.4	0.406^{T}
α-Pinene	60.2 ± 30.5	211.6 ± 94.7	0.470^{T}
Camphene	6.2 ± 3.5	40.2 ± 19.2	0.316^{U}
Sabinene	1.3 ± 1.0	1.6 ± 0.5	0.850^{U}
β-Pinene + Myrcene	178.6 ± 76.3	260.4 ± 68.4	0.533^{T}
α-Phellandrene	1.8 ± 0.9	4.5 ± 2.7	0.894^{U}
3-Carene	2.1 ± 0.7	37.9 ± 25.4	0.521^{U}
Limonene + β-Phellandrene	67.9 ± 34.9	134.6 ± 61.2	0.771^{T}
1,8-Cineole	1.6 ± 0.7	1.2 ± 0.3	0.506^{T}
γ-Terpinene	0.4 ± 0.3	3.7 ± 2.7	0.491^{U}
Terpinolene	0.8 ± 0.8	14.6 ± 9.8	0.319^{U}
Alloocimene	0.0 ± 0.0	0.4 ± 0.2	0.245^{U}
Camphor	0.4 ± 0.2	1.1 ± 0.3	0.149^{T}
Pinocarvone	0.0 ± 0.0	0.9 ± 0.6	0.444^{U}
Borneol	0.3 ± 0.2	0.4 ± 0.2	1.000^{U}
Terpinen-4-ol	1.3 ± 0.4	0.5 ± 0.3	**0.023**^{U}
α-Terpineol	6.9 ± 2.7	1.8 ± 0.9	**0.017**^{T}
Myrtenal	0.5 ± 0.2	1.0 ± 0.5	0.677^{U}
Bornyl acetate	7.6 ± 3.8	10.8 ± 6.4	0.599^{U}
Sesquiterpenes			
α-Copaene	0.4 ± 0.1	0.4 ± 0.2	0.954^{U}
Longifolene	1.9 ± 0.7	1.1 ± 0.3	0.170^{U}
(*E*)-β-caryophyllene	2.2 ± 1.1	1.0 ± 0.3	0.103^{U}
(*E*)-β-farnesene	0.0 ± 0.0	0.4 ± 0.3	0.529^{U}
α-Humulene	1.4 ± 0.9	0.0 ± 0.0	**0.007**^{U}
δ-Cadinene	3.2 ± 1.0	1.5 ± 0.5	0.101^{T}
α-Cubebene	0.5 ± 0.2	0.5 ± 0.2	0.698^{U}
Longipinene	1.1 ± 0.3	0.5 ± 0.1	**0.046**^{T}
α-Ylangene	1.0 ± 0.5	0.9 ± 0.4	0.677^{U}
Longicyclene	0.3 ± 0.1	0.2 ± 0.1	0.289^{T}
β-Bourbonene	2.7 ± 0.9	0.1 ± 0.1	**0.001**^{U}
Isoledene	1.9 ± 0.9	2.2 ± 1.2	0.426^{U}
β-Selinene	0.3 ± 0.1	0.2 ± 0.1	0.235^{U}
Undentified sesquiterpene 1	1.6 ± 0.5	0.3 ± 0.2	**0.004**^{U}
Undentified sesquiterpene 2	1.2 ± 0.6	0.0 ± 0.0	**0.007**^{U}
(*E,E*)-α-farnesene	0.0 ± 0.0	2.8 ± 0.7	**<0.000**^{T}
Germacrene-D	2.2 ± 1.4	0.0 ± 0.0	**0.007**^{U}
Undentified sesquiterpene 3	1.2 ± 0.6	0.2 ± 0.2	**0.030**^{U}
α-Cedrene	0.3 ± 0.3	0.5 ± 0.3	0.909^{U}
Undentified sesquiterpene 4	0.2 ± 0.2	0.4 ± 0.2	0.720^{U}
Undentified sesquiterpene 5	0.2 ± 0.2	0.4 ± 0.3	1.000^{U}
γ-Cadinene	1.2 ± 0.4	0.0 ± 0.0	**0.001**^{U}
Green leaf volatiles			
Cis-3-hexenyl isovaleric	0.0 ± 0.0	0.5 ± 0.3	0.529^{U}
Cis-3-hexenyl tiglate	0.0 ± 0.0	0.8 ± 0.4	0.444^{U}
Nonanal	26.3 ± 10.2	7.7 ± 0.9	0.103^{U}
Methyl salicylate	0.0 ± 0.0	2.1 ± 1.0	0.444^{U}

[a] VOC emissions were measured from the bark surfaces of control (CT_{Iitti}, n = 4) and beetle attacked (BAT_{Iitti}, n = 12) Norway spruce trees at Iitti site in June 2011. T = Independent Sample T-Test, U = Mann–Whitney U Test. The β-pinene and myrcene were coeluted in the chromatography and the same case was for limonene and β-phellandrene so they are not separated to maintain the precision. **Emboldened value** represents significant differences. VOC emissions data was temperature standardized at 20 °C.

Table 3
Mean (±SE) VOC emissions from bark surface of Norway spruce trees at Kuopio and Iitti site in August 2011.[a]

Emission (μg h^{-1} m^{-2} (bark area))	CT_{Kuopio}	BAT_{Iitti}	P-value
Monoterpenes			
Tricyclene	0.0 ± 0.0	0.9 ± 0.5	0.288^{U}
α-Pinene	1.6 ± 0.4	62.8 ± 23.6	**0.002**^{U}
Camphene	0.2 ± 0.1	11.1 ± 4.4	**0.001**^{U}
Sabinene	0.0 ± 0.0	2.8 ± 1.3	0.288^{U}
β-Pinene + Myrcene	5.4 ± 2.0	105.0 ± 66.4	0.162^{U}
α-Phellandrene	0.0 ± 0.0	0.5 ± 0.2	0.288^{U}
3-Carene	1.8 ± 0.2	4.0 ± 1.2	0.163^{U}
Limonene	1.2 ± 0.3	17.0 ± 6.0	**0.002**^{U}
β-Phellandrene	1.1 ± 0.4	8.7 ± 5.0	0.477^{U}
1,8-Cineole	0.0 ± 0.0	1.0 ± 0.4	**0.011**^{U}
γ-Terpinene	0.0 ± 0.0	0.3 ± 0.2	1.000^{U}
Terpinolene	0.0 ± 0.0	1.4 ± 0.9	0.541^{U}
Camphor	0.1 ± 0.1	0.6 ± 0.2	0.182^{U}
Borneol	0.0 ± 0.0	0.3 ± 0.1	0.288^{U}
Terpinen-4-ol	0.1 ± 0.1	0.3 ± 0.2	1.000^{U}
α-Terpineol	0.0 ± 0.0	0.4 ± 0.2	0.487^{U}
Bornyl acetate	0.4 ± 0.1	1.7 ± 0.4	**0.001**^{T}
Sesquiterpenes			
α-Copaene	0.0 ± 0.0	0.1 ± 0.1	0.487^{U}
Longifolene	0.9 ± 0.1	0.8 ± 0.2	0.907^{T}
(*E*)-β-caryophyllene	0.0 ± 0.0	0.2 ± 0.2	0.541^{U}
(*E*)-β-farnesene	0.5 ± 0.5	0.8 ± 0.5	1.000^{U}
α-Humulene	0.6 ± 0.4	0.3 ± 0.2	0.371^{U}
α-Cubebene	0.0 ± 0.0	0.1 ± 0.1	1.000^{U}
Longipinene	0.0 ± 0.0	0.0 ± 0.0	1.000^{T}
α-Ylangene	0.0 ± 0.0	0.2 ± 0.1	0.288^{U}
Longicyclene	0.0 ± 0.0	0.1 ± 0.0	0.487^{U}
β-Bourbobene	0.0 ± 0.0	0.1 ± 0.1	1.000^{U}
Isoledene	0.0 ± 0.0	0.7 ± 0.2	**0.026**^{T}
Unidentified sesquiterpene 1	0.0 ± 0.0	0.1 ± 0.1	1.000^{U}
Germacrene-D	0.0 ± 0.0	0.3 ± 0.3	1.000^{U}
Nonanal	1.5 ± 0.1	2.8 ± 0.2	**<0.000**^{T}

[a] VOC emissions were measured from the bark surfaces of control (CT_{Kuopio}, n = 4) Norway spruce trees at Kuopio site outside the outbreak area and beetle attacked (BAT_{Iitti}, n = 11) spruce trees at Iitti site in August 2011. T = Independent Sample T-Test, U = Mann–Whitney U Test. The β-pinene and myrcene were coeluted in the chromatography so they are not separated to maintain the precision. **Emboldened value** represents significant differences. VOC emissions data was temperature standardized at 20 °C.

common fungal associate of I. typographus as described by Baier et al. (2002).

Effect of bark-beetle damage on BVOC emissions is likely to be higher in bark than foliage. Namely, the monoterpene content in the needle tissues of conifers is known to be lower than in the bark (Lusebrink et al., 2011). Compared to the trunks, the total amount of extractable monoterpenes emitted from the foliage was one-third in lodgepole pine (*P. contorta*) and a half in interior spruce (*Piceaengelmannii* × *glauca*) (Pureswaran et al., 2004). Moreover, pine weevil feeding on Scots pine seedlings increased bark emission of monoterpenes by nearly 4-fold compared to the increase in needle emissions by 2.8-fold (Heijari et al., 2011). Nevertheless, more extensive measurement campaigns are needed in order to estimate the effects of bark-beetle attack on total BVOC emissions at tree level, including the measurements from foliage and trunk. A considerable increase in the emissions of α-pinene and camphene at Iitti site in August indicated a higher yield and storage of defensive MTs in the spruce trunks attacked by bark beetles (Leufvén and Birgersson, 1987). The higher emission of α-pinene from the spruce trunks of Iitti site in August could also synergistically influence the attraction of *I. typographus* to their aggregation pheromones resulting in a higher attack rate caused by an increased number of bark beetles (Erbilgin et al., 2007).

The monoterpene, myrcene with 21-fold higher emissions in beetle attacked spruce trunks at Lahti, is an important defense compound induced also from the trunk of mature lodgepole × jack pine hybrids inoculated with mountain pine beetles (Lusebrink et al., 2013). A 5.5-fold increase of tricycle emission was reported in the bark of Norway spruce stands inoculated with *I. typographus*-associated *C. polonica* (Baier et al., 2002), which is nearly the same as the emission rate of tricyclene induced from beetle-attacked spruce stands at Lahti site in August. The emission of different MTs in different years and different provenances (e.g. Iitti in 2011, Lahti in 2012) may be caused partly by MT genotype and partly by the storage of large amount of MT hydrocarbons (especially oxygenated MTs) in Norway spruce after active photosynthesizing phase during the growing season (particularly in August). The potential site for the storage of MT-hydrocarbons is in the gallery walls of phloem in Norway spruce trunk and this storage is

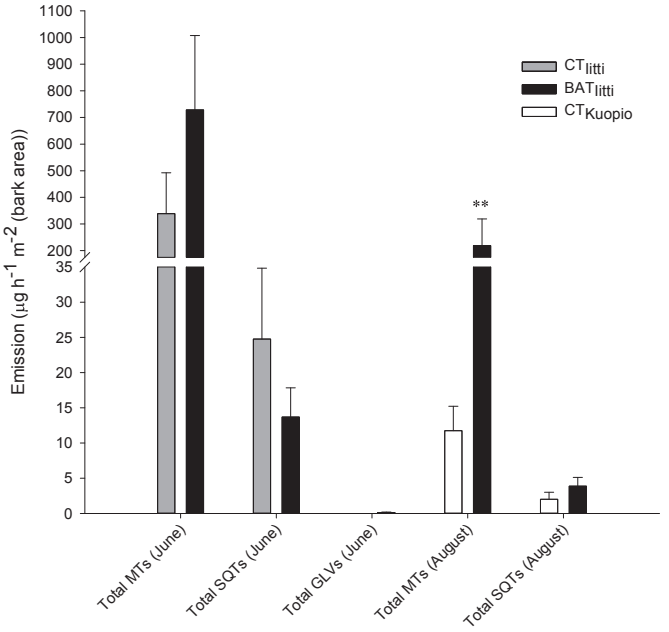

Fig. 1. Mean (+SE) emissions of total monoterpenes (MTs) (June and August), total sesquiterpenes (SQTs) (June and August) and total green leaf volatiles (GLVs) (June only) measured from Norway spruce bark surface of bark beetle-attacked trees at litti (BAT_{litti}, n = 12 in June, n = 11 in August), control trees at litti (CT_{litti}, n = 4 in June) and control trees at Kuopio (CT_{Kuopio}, n = 4 in August) in 2011. Significant difference between BAT_{litti} and CT_{Kuopio} in August is indicated by **p < 0.01 (independent samples t-test). Note break on y-axis. BVOC emissions data was temperature standardized at 20 °C.

Table 4
Mean (±SE) VOC emissions from bark surfaces of Norway spruce trees at Lahti site in June 2012.[a]

Emission (µg h^{-1} m^{-2} (bark area))	CT	BAT	P-value
Monoterpenes			
Tricyclene	0.8 ± 0.3	0.5 ± 0.3	0.313[U]
α-Pinene	5.5 ± 1.2	32.6 ± 14.6	0.114[U]
Camphene	6.1 ± 1.8	3.6 ± 1.6	0.211[T]
Sabinene	0.3 ± 0.2	0.9 ± 0.4	0.248[U]
β-Pinene	2.5 ± 0.5	24.5 ± 12.5	0.118[U]
Myrcene	0.8 ± 0.3	1.4 ± 0.7	0.911[U]
3-Carene	0.6 ± 0.1	0.9 ± 0.2	0.346[U]
Limonene	2.8 ± 0.8	3.2 ± 1.2	0.922[T]
β-Phellandrene	0.0 ± 0.0	1.2 ± 0.5	**0.029**[U]
1,8-Cineole	0.1 ± 0.1	0.1 ± 0.1	0.931[U]
Green leaf volatiles			
Cis-3-hexenyl-acetate	0.4 ± 0.3	0.8 ± 0.4	0.343[U]
Nonanal	6.0 ± 0.7	5.7 ± 0.5	0.737[T]

[a] VOC emissions were measured from the bark surface of control (CT, n = 11) and beetle attacked (BAT, n = 10) Norway spruce trees from the urban forest sites at Lahti in June 2012. T = Independent Sample T-Test, U = Mann–Whitney U Test. **Emboldened value** represents significant differences.

Table 5
Mean (±SE) VOC emissions from bark surfaces of Norway spruce trees at Lahti site in August 2012.[a]

Emission (µg h^{-1} m^{-2} (bark area))	CT	BAT	P-value
Isoprene	13.5 ± 6.5	10.9 ± 3.5	0.207[U]
Monoterpenes			
Tricyclene	0.4 ± 0.1	1.9 ± 0.9	**0.036**[U]
α-Pinene	5.0 ± 1.4	180.5 ± 167.7	0.591[U]
Camphene	3.0 ± 0.7	8.5 ± 2.0	**0.004**[T]
Sabinene	0.5 ± 0.1	7.8 ± 6.8	0.084[U]
β-Pinene	2.3 ± 0.9	119.1 ± 111.3	0.353[U]
Myrcene	0.7 ± 0.2	15.1 ± 12.5	**0.031**[U]
3-Carene	0.8 ± 0.1	1.1 ± 0.5	0.620[T]
Limonene	1.9 ± 0.4	8.7 ± 6.2	0.303[U]
β-Phellandrene	0.3 ± 0.1	25.0 ± 23.6	0.258[U]
1,8-Cineole	0.3 ± 0.1	1.1 ± 0.4	**0.013**[U]
Camphor	0.0 ± 0.0	0.5 ± 0.3	**0.048**[U]
α-Terpineol	0.0 ± 0.0	0.5 ± 0.4	**0.048**[U]
Green leaf volatiles			
Cis-3-hexenyl-acetate	0.7 ± 0.4	1.9 ± 0.7	0.107[U]
Nonanal	2.6 ± 0.6	3.2 ± 1.3	0.529[U]

[a] VOC emissions were measured from the bark surface of control (CT, n = 16) and beetle attacked (BAT, n = 5) Norway spruce trees from the urban forest sites at Lahti in August 2012. T = Independent Sample T-Test, U = Mann–Whitney U Test. **Emboldened value** represents significant differences.

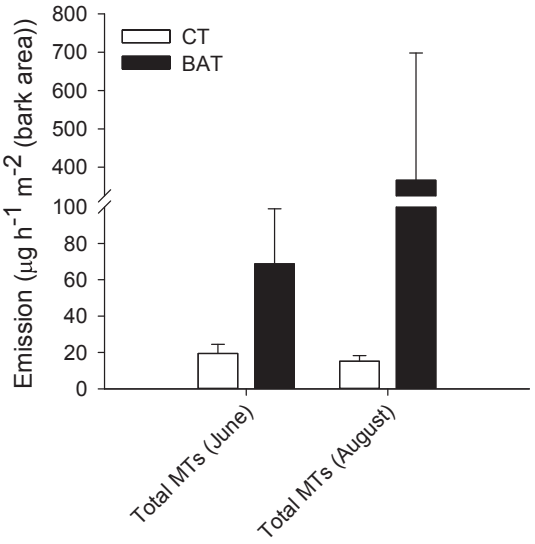

Fig. 2. Mean (+SE) emissions of total monoterpenes (MTs) measured from Norway spruce trees of urban-forest stands at Lahti. The emissions were measured from the bark surface of control (CT, n = 11) and beetle attacked (BAT, n = 10) trees in June 2012, and of control (CT, n = 16) and beetle attacked (BAT, n = 5) trees in August 2012. Note break on y-axis. BVOC emissions data was temperature standardized at 20 °C.

frequently attacked by the bark beetles (Leufvén and Birgersson, 1987).

Our study suggested a positive correlation of the mean trap catch of bark beetles with α-pinene emission, a predominant monoterpene of Norway spruce. This result is in agreement with an increased capture of *I. typographus* in pheromone traps with increased emission of α-pinene in the traps in clear cut areas surrounded by Norway spruce stands at Ås, southeast of Norway (Erbilgin et al., 2007). Therefore, we can suggest that higher attack rate by a large number of bark beetles on spruce tree trunk results in the higher emissions of MTs from the trunk. These observations also suggest that pheromone trap catch could serve as a practical indicator to predict MT emissions of a conifer tree stand for modelling purposes.

Epiphytic lichens can absorb and release semi-volatiles (Schrlau et al., 2011) and may act as an external storage of MTs on tree stems. The monoterpene, limonene can be absorbed by neighboring non-emitting plants (Noe et al. 2008). Therefore, two MTs (limonene and 1,8-cineole) correlating with epiphytic lichen cover could be at least partly released from the epiphytic lichens during BVOC sampling and originated from various sources. This should be considered when sampling VOCs from tree trunks densely covered by lichens.

Bark beetle damage greatly influenced the BVOC emissions from bark at breast height (ca. 1.3 m from ground level) of mature

Norway spruce trees in our study. Earlier it was shown that constitutive emission of MTs from 1 cm^2 of fresh resin drop is four-fold higher than the emissions from equivalent needle area at branch level (Eller et al., 2013). Our study didn't focus on the emission from resin drops (Eller et al., 2013) and foliage (Martin et al., 2003) of spruce trees, but instead provided clear information on bark level emissions under different conditions, e.g. from bark beetle induced phloem and cambium emissions, and epiphytic lichen cover. Therefore, the partial picture obtained from this study may be helpful for the consideration of bark beetle outbreaks as biotic stressors in BVOC emission models such as MEGAN (Guenther et al., 2012). Our BVOC sampling effort was limited on breast height level like previously reported by Amin et al. (2013). Thus, more comprehensive efforts are still needed to get reliable data of whole trunk bark and foliage scale BVOC emissions of attacked trees.

5. Conclusions

Bark beetle attack increases the emissions of MTs from the bark surfaces of Norway spruce, however an extensive induction of defensive MT compounds results in an ultimate reduction of SQTs biosynthesis in the tree trunk. An increased emission rate of α-pinene from the spruce trunk may serve as an indicator for the increased colonization rate of bark beetles resulting in an extensive bark beetle pressure in Norway spruce forest. In addition to α-pinene, camphene and myrcene are other dominant MTs induced in a considerable amount from the bark surfaces of Norway spruce trees under bark beetle stress. We can conclude that bark beetle outbreaks affect local BVOC emissions from conifer forests, which suggest that the impacts of insect outbreaks are worth of consideration to global BVOC emission models.

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