Terpenoid and carbonyl emissions from Norway spruce in Finland during the growing season

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Abstract. We present spring and summer volatile organic compound (VOC) emission rate measurements from Norway spruce (*Picea abies* L. Karst) growing in a boreal forest in southern Finland. The measurements were conducted using in situ gas-chromatograph with 1to 2-hour time resolution to reveal quantitative and qualitative short-term and seasonal variability of the emissions. The measurements cover altogether 14 weeks in years 2011, 2014 and 2015. Monoterpene (MT) and sesquiterpene (SQT) emission rates were measured all the time, but isoprene only in 2014 and 2015 and acetone and C_4-C_{10} aldehydes only in 2015. The emission rates of all the compounds were low in spring, but MT, acetone and C_4-C_{10} aldehydes emission rates increased as summer proceeded, reaching maximum emission rates in July. Late summer mean values (late July and August) were 29, 17 and 33 ng g(dw)$^{-1}$ h^{-1} for MTs, acetone and aldehydes respectively. SQT emission rates increased during the summer and highest emissions were measured late summer (late summer mean value 84 ng g(dw)$^{-1}$ h^{-1}) concomitant with highest linalool emissions most likely due to stress effects. The between-tree variability of emission pattern was studied by measuring seven different trees during the same afternoon using adsorbent tubes. Especially the contributions of limonene, terpinolene and camphene were found to vary between trees, whereas proportions of α- and β-pinene were more stable. Our results show that it is important to measure emissions on canopy level due to irregular emission pattern, but reliable SQT emission data can be measured only from enclosures. SQT emissions contributed more than 90 % of the ozone reactivity most of the time, and about 70 % of the OH reactivity during late summer. The contribution of aldehydes to OH reactivity was comparable to the one of MT during late summer, 10 %-30 % most of the time.

1 Introduction

The boreal forest is the largest terrestrial biome, forming an almost continuous belt around the northern hemisphere. The boreal forest zone is characterized by a short growing season and a limited number of tree species. The most common tree species are Scots pine, Norway spruce and silver and downy birch and they produce and emit vast amounts of biogenic volatile organic compounds (VOCs) (Bourtsoukidis et al., 2014a, b; Bäck et al., 2012; Cojocariu

37   et al., 2004; Grabmer et al., 2006; Hakola et al., 2001, 2006; Tarvainen et al., 2005; Yassaa et al., 2012). The

38   compounds are mainly isoprene, monoterpenes (MT), sesquiterpenes (SQT) and oxygenated volatile organic

39   compounds (OVOCs) (Tarvainen et al., 2007). There is a variety of factors controlling these emission, both biotic

40   (Pinto-Zevallos et al., 2013; Joutsensaari et al., 2015) and abiotic stress (Vickers et a., 2009; Bourtsoukidis et al.,

41   2012; Bourtsoukidis et al., 2014c) factors can initiate or alter VOC emissions. Abiotic stress factors have been

42   reviewed by Loreto and Schnizler (2010). Terpenes for example relieve oxidative and thermal stresses of trees. Many

43   stress factors can also interact and cause additive effects (Niinemets, 2010; Holopainen and Gershenzon, 2010).

44   Biotic stresses such as acarid species infestation have been shown to initiate farnesene and linalool emissions in

45   spruce seedlings (Kännaste et al., 2008). Emission potentials and composition varies a lot between different tree

46   species (Guenther et al. 2012). However, there is also a lot of variation in the emissions of different individuals of the

47   same tree species. Bäck et al. (2012) showed that Scots pine trees of the same age, growing in the same environment,

48   emit very different monoterpene selections. These so called different chemotypes cause uncertainties in emission

49   modelling.

50   In the atmosphere VOCs are oxidized, which affects the tropospheric ozone formation (Chameides et al., 1992) and

51   contribute to the lifetime of methane by consuming hydroxyl radicals. In addition reaction products of VOCs also

52   participate in the formation and growth of new particles (Tunved et al., 2006). In smog chamber studies secondary

53   organic aerosol (SOA) yields for different hydrocarbons and even for different MTs have been found to vary

54   considerably (Griffin et al., 1999). Jaoui et al. (2013) studied SOA formation from SQT and found that the high

55   reactivity of SQT produced generally high conversion into SOA products. Furthermore, they found that the yields were

56   dependent on the oxidant used and were highest for nitrate radical (NO_3) reactions. Of the SQT acidic products, only

57   β-caryophyllinic acid has been observed in ambient samples (Jaoui et al., 2013; Vestenius et al., 2014). Due to their

58   high reactivity, SQT are not usually found in ambient air. Hakola et al. (2012) detected longifolene and isolongifolene

59   in boreal forest air during late summer. Hence, the best way to evaluate the atmospheric impact of SQTs is to measure

60   them from emissions.

61   In addition to isoprene and MTs and SQTs, plants emit also large amounts of oxygenated compounds i.e. alcohols,

62   carbonyl compounds and organic acids (Koppmann and Wildt, 2007). OVOCs containing six carbon atoms (C_6) are

63   emitted directly by plants often as a result of physical damage (Fall et al., 1999; Hakola et al., 2001). Saturated

64   aldehydes (hexanal, heptanal, octanal, nonanal, and decanal) have also been found in direct emissions of plants (Wildt

65   et al., 2003) as well as methanol, acetone and acetaldehyde (Bourtsoukidis et al. 2014b).

66   In the present study we conducted on-line gas-chromatographic measurements of emissions of MTs and SQTs as well

67   as C_4-C_{10} saturated aliphatic carbonyls from Norway spruce (*Picea abies* L. Karst) branches. Although Norway spruce

68   is one of the main forest tree species in Central and Northern Europe, there are relatively limited amount of data on its

69   emissions (Hakola et al., 2003; Grabmer et al., 2006; Bourtsoukidis et al., 2014a and b, Yassaa et al. 2012). Rinne et

70   al. (2009) identified knowledge gaps concerning VOC emissions from boreal environment and concluded that there is

71   a lack of knowledge in non-terpenoid emissions from most of the boreal tree species. They also pointed out that

72   chemotypic variations are not well enough understood to be taken into account in emission modelling. To fill this

knowledge gap we conducted BVOC emission measurements from Norway spruce. On-line gas-chromatograph mass spectrometer (GC-MS) was chosen because in addition to detection of individual MTs it allows sensitive detection of SQTs, which is often difficult to perform under field conditions. The on-line measurements were considered essential for evaluating the factors affecting emission rates, for example their temperature and light dependence. Our campaigns cover periods of years 2011, 2014 and 2015 during spring and summer, altogether about 14 weeks. In 2015 also carbonyl compounds were added to the measurement scheme, since there is no earlier data of their emissions.

2 Methods

2.1 VOC measurements

The measurements were conducted at the SMEAR II station (Station for Measuring Forest Ecosystem-Atmosphere Relations, 61^051'N, 24^018'E, 181 a.s.l) in Hyytiälä, southern Finland (Hari and Kulmala 2005) in 2011, 2014, and 2015. The measurements took place in spring/early summer 2011 (two weeks in April, five days in May and three days in June), spring/summer 2014 (one week in May, two weeks in June and one week in July), and summer 2015 (one week in June and two weeks in August) and they were conducted using an in situ gas-chromatograph.

Two different trees were measured; tree 1 in 2011 and tree2 in 2014 and 2015. The selected trees were growing in a managed mixed conifer forest (average tree age ca 50 years), and located about 5 meters from the measurement container. The height of the tree 1 in 2011 was about 10 meters (age about 40 years). The measured branch was a fully sunlit, healthy lower canopy branch pointing towards a small opening at about 2 meters height. In 2014 and 2015 a younger tree (tree 2, ca. 1 m tall, age ca 15 years) about 5 meters away from the tree used in 2011 was selected for the study. The branches were placed in a Teflon enclosure and the emission rates were measured using a dynamic flow through technique. The setup is shown in supporting material. The volume of the cylinder shape transparent Teflon enclosure was approximately 8 litres and it was equipped with inlet and outlet ports and a thermistor (Philips KTY 80/110, Royal Philips Electronics, Amsterdam, Netherlands) covered with Teflon tubing inside the enclosure. The photosynthetically active photon flux density (PPFD) was measured just above the enclosure by quantum sensor (LI-190SZ, LI-COR Biosciences,Lincoln, USA).

The flow through the enclosure was kept at about 3-5 litres min^{-1}. Ozone was removed from the incoming air using manganese oxide (MnO_2) coated copper nets. The emission rates were measured using the on-line GC-MS. From the enclosure outlet port air was directed through the 6 m long fluorinated ethylene propylene (FEP) inlet line (i.d. 1/8 inch) to the GC-MS with the flow of ~0.8 L/min. Subsamples were taken from this main flow with the flow of 40-60 ml/min directly into the cold trap of a thermal desorption unit (Perkin Elmer ATD-400) packed with Tenax TA in 2011 and Tenax TA/Carbopack-B in 2014 and 2015. The trap material was changed since isoprene was found not to be retained fully in the cold trap in 2011. The trap was kept at 20^0C during sampling to prevent water vapour present in the air from accumulating into the trap. The thermal desorption instrument was connected to a gas chromatograph (HP 5890) with DB-1 column (60 m, i.d. 0.25 mm, f.t. 0.25 μm) and a mass selective detector (HP 5972). One 20-minutes

106 sample was collected every other hour. The system was calibrated using liquid standards in methanol injected on Tenax

107 TA-Carbopack B adsorbent tubes. The detection limit was below 1 pptv for every MT- and SQT.

108 The following compounds were included in the calibration solutions: 2-methyl-3-buten-2-ol (MBO) (Fluka), camphene

109 (Aldrich), 3-carene (Aldrich), p-cymene (Sigma-Aldrich), 1,8-cineol (Aldrich), limonene (Fluka), linalool (Aldrich),

110 myrcene (Aldrich), α-pinene (Sigma-Aldrich), β-pinene (Fluka), terpinolene (Fluka), bornylacetate (Aldrich),

111 longicyclene (Aldrich), isolongifolene (Aldrich), β-caryophyllene (Sigma), aromadendrene (Sigma-Aldrich), α-

112 humulene (Aldrich), β-farnesene (Chroma Dex). Isoprene was calibrated using gaseous standard from National

113 Physical Laboratory (NPL). We had no standard for sabinene and therefore it was quantified using the calibration curve

114 of β-pinene, because both species elute close each other and their mass spectra are similar. Therefore the results for

115 sabinene are only semi-quantitative, but it enables the observations of diurnal and seasonal changes. Compared to off-

116 line adsorbent methods this in situ GC-MS had clearly lower background for carbonyl compounds and in 2015 we

117 were able to measure also acetone/propanal and C_4-C_{10} aldehyde emission rates. The aldehydes included in the

118 calibration solutions were: butanal (Fluka), pentanal (Fluka), hexanal (Aldrich), heptanal (Aldrich), octanal (Aldrich),

119 nonanal (Aldrich) and decanal (Fluka). Unfortunately, acetone co-eluted with propanal and the calibration was not

120 linear due to high acetone background in adsorbent tubes used for calibrations.

121 **2.2 Calculation of emission rates**

122 The emission rate is determined as the mass of compound per needle dry weight and per time according to

123

124 $$E = \frac{(C_2 - C_1)F}{m} \qquad\qquad (1)$$

125

126 Here C_2 is the concentration in the outgoing air, C_1 is the concentration in the incoming air, and F is the flow rate

127 into the enclosure. The dry weight of the biomass (m) was determined by drying the needles and shoot from the

128 enclosure at 75 ºC for 24 hours after the last sampling date. We also measured needle leaf areas and the specific leaf

129 area SLA is 136 m^2 g^{-1}.

130 **2.3 Emission potentials**

131 A strong dependence of biogenic VOC emissions on temperature has been seen in all emission studies of isoprene,

132 MTs, and SQTs (e.g. Kesselmeier and Staudt 1999; Ciccioli et al. 1999; Hansen and Seufert 2003; Tarvainen et al.

133 2005; Hakola et al. 2006). The temperature dependent pool emission rate is usually parameterized using a log-linear

134 formulation

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$$E(T) = E_S \exp(\beta(T - T_S)) \tag{2}$$

138

where $E(T)$ is the emission rate (µg g^{-1} h^{-1}) at leaf temperature T and β is the slope $\frac{d\,lnE}{dT}$ (Guenther et al. 1993). E_S is the emission rate at standard temperature T_S (usually set at 30 °C). The emission rate at standard temperature is also called the emission potential of the plant species, and while it is sometimes held to be a constant it may show variability related to e.g. season or the plant developmental stage (e.g. Hakola et al. 1998, 2001, 2003, 2006; Tarvainen et al. 2005, Aalto et al 2014).

Besides the temperature-dependent nature of the biogenic emissions, light dependence has been discovered already in early studies of plant emissions (e.g. the review of biogenic isoprene emission by Sanadze 2004 and e.g. Ghirardo et al 2010). The effect of light on the emission potentials is based on the assumption that the emissions follow similar pattern of saturating light response which is observed for photosynthesis, and the formulation of the temperature effect is adopted from simulations of the temperature response of enzymatic activity. The algorithm formulation is given e.g. in Guenther et al. 1993 and Guenther 1997.

In this work we have carried out nonlinear regression analysis with two fitted parameters, arriving at individual standard emission rates and slope values for the modelled MTs and SQTs compounds during each model period. The compounds analysed with the temperature dependent pool emission rate were the most copiously emitted MTs and SQTs, other MTs, other SQTs, acetone and sum of aldehydes. The light and temperature controlled instant emission rates were obtained for isoprene. An alternative modelling approach was tested using a hybrid emission algorithm, which has both the temperature-dependent pool emission and the light and temperature controlled instant emission terms.

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2.4 Chemotype measurements

In order to estimate the between-tree variability of the emissions, we conducted a study in 2014, where we made qualitative monoterpene analysis from six different spruces (trees 3-8) growing in a same area not farther than about 10 metres from each other. All the trees were about 1 m high and naturally regenerated from local seeds. A branch was enclosed in a Teflon bag and after waiting for 5 minutes we collected a 5 minute sample on a Tenax TA/Carbopack-B tube and analysed later in a laboratory using Perkin-Elmer thermodesorption instrument (Turbomatrix 650) connected to Perkin-Elmer gas-chromatograph (Clarus 600) mass spectrometer (Clarus 600T) with DB-5 column. The samples were taken during one afternoon on 24 June 2014.

2.4 Calculating the reactivity of the emissions

169 We calculated the total reactivity of the emissions ($TCRE_x$) by combining the emission rates (E_i) with reaction rate
170 coefficients ($k_{i,x}$).

171 $$TCRE_x = \sum E_i \, k_{i,x} \tag{3}$$

172 This determines approximately the relative role of the compounds or compound classes in local OH, and O_3
173 chemistry. The reaction rate coefficients are listed in Table 1. When available, temperature-dependent rate
174 coefficients have been used. When experimental data was not available, the reaction coefficients have been estimated
175 with the AopWin™ module of the EPI™ software suite (https://www.epa.gov/tsca-screening-tools/epi-suitetm-
176 estimation-program-interface, EPA, U.S.A).

177 **3. Results and discussion**

178 **3.1 Weather patterns during the measurements**

179 According to the statistics of the Finnish Meteorological Institute, the weather conditions in Finland were close to
180 normal during the growing season in the years the measurements were carried out. The main features of the weather
181 patterns are characterised here briefly to provide an average estimate of the conditions in the measurement years
182 compared with the long-term average conditions in Finland.

183 In 2011, the spring was early and warm. Thermal spring (mean daily temperature above 0°C) started in the whole
184 country during the first few days of April. The average temperatures were higher than the normal long-term average
185 temperatures. In addition to the warm temperatures, April had very little precipitation. The same pattern continued in
186 May, with slightly higher temperatures than the normal long-term average. Towards the end of the month the weather
187 turned more unstable, with more rains and cooler night temperatures. The average temperature in June was a little over
188 two degrees higher than the normal long-term average, and there were some intense thunderstorms.

189 In 2014, the weather conditions in May were quite typical, with the average temperatures close to the long-term average
190 values in all parts of the country. The month started with temperatures cooler than the long-term average, and the cool
191 period continued for about three weeks. After the cool period the weather became warmer with a south-eastern air
192 flow, and hot (over 25°C) air temperatures were observed in southern and central parts of the country. Towards the
193 end of May, cooler air spread over the country from the northeast, and the temperature drops could be high in eastern
194 Finland. May was also characterised with precipitation, especially in eastern Finland. June started with a warm spell,
195 but towards the end the weather was much cooler, with the average temperatures 1 to 2 degrees lower than the long-
196 term average. The precipitation was regionally quite variable in June, the amount could be doubly the long-term
197 average in some areas, while the amounts were only half of it in many places in central Finland. July was much warmer
198 than the long-term average temperatures, especially in western Finland and in Lapland. July also had very little rain.

199 In 2015, the June average temperatures were 1 to 2 degrees below the long-term averages, especially in the western

200 parts of central Finland, and southern Lapland. There were also more rain showers than normally. In July the cold spell

201 and rainy days continued, with the average temperatures below the long-term averages, especially in the eastern parts

202 of the country. Highest precipitation rates were measured in the southern and western coastal regions, and in the eastern

203 parts of the country. In August the warmth returned after two cooler months, with average temperatures 1 to 2 degrees

204 above the long-term average values. August also had very little rain, except for some parts in eastern Finland and in

205 Lapland.

206 The observed mean temperature and precipitation amounts at the Juupajoki weather station in Hyytiälä during each

207 measurement month in 2011, 2014, and 2015 are shown in Table 2.

208 **3.2 Variability of the VOC emissions**

209 Seasonal mean emission rates of isoprene, 2-methyl-3-buten-2-ol (MBO), MTs and SQTs are presented in Table 3

210 and Fig 1. Typical diurnal variations of the most abundant compounds for each season are shown in Fig. 2. Since

211 most of the emission rates of the measured compounds were higher in late summer than in early summer, we

212 calculated the spring (April and May), early summer (June to mid-July) and late summer (late July and August) mean

213 emissions separately. This describes the emission rate changes better than monthly means.

214 Isoprene emission rates were low in spring and early summer, but increased in August. In spring emission rates were

215 below detection limit most of the time and early and late summer means were 1.3 ± 3.7 and 6.0 ± 12 ng g(dry weight)$^{-1}$

216 h^{-1}, respectively. The highest daily maxima isoprene emissions were about 70-80 ng g(dw)$^{-1}$ h^{-1}, but usually they

217 remained below 20 ng g(dw)$^{-1}$ h^{-1}. Our measured values (Table 3) match very well with the measurements by

218 Bourtsoukidis et al (2014b) who report season medians varying from 1.6 ng g(dry weight)$^{-1}$ h^{-1} in autumn to 3.7 ng

219 g(dry weight)$^{-1}$ h^{-1} in spring. However, while the highest emission rates were measured in late summer in the present

220 study, Bourtsoukidis et al. (2014b) found highest emission rates in spring.

221 MT emission rates were below 50 ng g(dw)$^{-1}$ h^{-1} most of the time in April, May and still in the beginning of June for

222 every measurement year, below 50 ng g(dw)$^{-1}$ h^{-1} most of the time. At the end of June the MT emission rates started to

223 increase (about 30 %) to the level where they remained until the end of August, the daily maxima or their sum

224 remaining below 300 ng g(dw)$^{-1}$ h^{-1}. In comparison with the study by Bourtsoukidis et al. (2014b), MT emission rates

225 in Finland are four to ten times lower than those measured in Germany and their seasonal cycles are different. As with

226 isoprene, they measured the highest MT emission rates during spring, whereas our highest emissions take place late

227 summer. Median seasonal values reported by them are 203.1, 136.5 and 80.8 ng g(dw)$^{-1}$ h^{-1} for spring, summer and

228 autumn, respectively. Our averages are 8, 21 and 28 ng g(dw)$^{-1}$ h^{-1} for spring, early summer and late summer,

229 respectively (Table 3).

230 A substantial change in the emission patterns took place at the end of July, when SQT emission rates increased up to

231 3-4 times higher than the MT emission rates at the same time (Table 3). Such a change in emissions was not observed

232   in the study by Bourtsoukidis et al. (2014b).). Instead of late summer increase, they observed again highest emissions

233   already during the spring (118.6 and 64.9 ng g(dw)$^{-1}$ h^{-1} in spring and summer, respectively) after which emissions

234   significantly declined. Moreover, they report that MTs dominated the Norway spruce emissions through the entire

235   measuring period (April-November), SQT emission rates being equal to MT emission rates during spring, but only

236   about half of MT emission rates during summer and about 20 % during autumn. One potential explanation for such a

237   different seasonality and emission strengths may lie in the differences between site specific factors such as soil moisture

238   conditions, local climate (winter in Germany is much milder and the trees do not face as dramatic change as in Finland

239   when winter turns to spring), stand age or stress factors. The tree measured in Germany was much older (about 80

240   years). In a boreal forest, late summer normally is the warmest and most humid season favouring high emissions, as

241   was also the case in our study periods. On the contrary, in central Germany July was relatively cold and wet, and

242   according to the authors, reduced emissions were therefore not surprising (Boutsourkidis et al 2014b).

243   Another interesting feature can be seen in the specified emission rates of different compounds. In the present study the

244   main SQT in spruce emissions was β-farnesene. About 50% of the SQT emission consisted of β-farnesene and its

245   maximum emission rate (155 ng g(dw)$^{-1}$ h^{-1}) was measured on the afternoon of 31 July 2015. Two other identified

246   SQTs were β-caryophyllene and α-humulene. There were two more SQTs, which also contributed significantly to the

247   total SQT emission rates, but since no calibration standards were available for these , their quantification is only

248   tentative. Linalool emissions increased simultaneously with SQT emissions (Fig. 1) reaching maximum concentrations

249   during late summer in August, in the same way as was previously observed in the measurements of Scots pine

250   emissions in the same forest in southern Finland (Hakola et al., 2006), where emissions were found to increase late

251   summer concomitant with the maximum concentration of the airborne pathogen spores, and Hakola et al. (2006)

252   suggested a potential defensive role of the conifer linalool and SQT emissions. Several other reports point to similar

253   correlations between SQT (in particular β-farnesene) and oxygenated MTs such as linalool emissions and biotic

254   stresses in controlled experiments. For example, increases in farnesene, methyl salicylate (MeSA) and linalool

255   emissions were reported to be an induced response by Norway spruce seedlings to feeding damage by mite species

256   (Kännaste et al. 2009), indicating that their biosynthesis might prevent the trees from being damaged. Interestingly,

257   the release of β-farnesene seemed to be mite specific and attractive to pine weevils, whereas linalool and MeSA were

258   deterrents. Blande et al. (2009) discovered pine weevil feeding to clearly induce the emission of MTs and SQTs,

259   particularly linalool and (E)-β-farnesene, from branch tips of Norway spruce seedlings, Also, in a licentiate thesis of

260   Petterson (2007) linalool and β-farnesene were shown to be emitted due to stress. The emissions from Norway spruce

261   increased significantly after trees were treated with methyljasmonate (MeJA). Martin et al (2003) discovered that MeJA

262   triggered increases in the rate of linalool emission more than 100-fold and that of SQTs more than 30-fold. Emissions

263   followed a pronounced diurnal rhythm with the maximum amount released during the light period, suggesting that they

264   are induced de novo after treatment. Our study shows that such major changes in emission patterns can also occur in

265   trees in field conditions, and without any clear visible infestations or feeding, indicating that they probably are systemic

266   defence mechanisms rather than direct ones (Eyles et al 2010).

267   In 2015 we measured also acetone/propanal and C$_4$-C$_{10}$ aldehyde emission rates. The total amount of these measured

268   carbonyl compounds was comparable to the amount of MTs (Table 3) although with our method it was not possible to

269   measure emissions of the most volatile aldehydes, formaldehyde and acetaldehyde, which are also emitted from trees

270   in significant quantities (Cojocariu et al., 2004, Koppmann and Wildt, 2007; Bourtsoukidis et al., 2014b). In summer

271   2015 the carbonyl compounds consisted mainly of acetone (30 %), and the shares for the other compounds were as

272   follows: nonanal (21%), decanal (17%), heptanal (14%), hexanal (10%) and pentanal (5%). The shares of butanal and

273   octanal were less than 2% each. The seasonal mean values are shown in Table 3. Aldehydes with shorter carbon

274   backbones (butanal, pentanal, hexanal) have higher emissions in early summer like most MTs, while aldehyges with

275   longer carbon backbones (heptanal, octanal, nonanal, decanal) have higher emissions in late summer similarly to SQTs.

276   Diurnal variability of the emission rates of MT and SQT, acetone/propanal and larger aldehydes are shown in Fig.2.

277   They all show similar temperature dependent variability with maxima during the afternoon and minima in the night.

278   The SQT daily peak emissions were measured two hours later than MT and aldehyde peaks.

279

3.3 Tree to tree variability in emission pattern

281   When following the emission seasonality, we discovered that the MT emission patterns were somewhat different

282   between the two trees measured. The tree measured in 2011 (tree 1) emitted mainly α-pinene in May, whereas the tree

283   measured in 2014 and 2015 (tree 2) emitted mainly limonene in May (Table 4). As summer proceeded the contribution

284   of limonene emission decreased in both trees and the share of α-pinene increased in tree 2. The species specific Norway

285   spruce emissions have been measured earlier at least by Hakola et al. (2003) and Bourtsoukidis et al. (2014a). The

286   measurements by Hakola et al. covered all seasons, but only a few daytime samples for each season, whereas the

287   measurements by Bourtsoukidis et al. covered three weeks in September-October in an Estonian forest. The main MTs

288   detected in the Estonian forest were α-pinene (59 %) and 3-carene (26 %), but also camphene, limonene, β-pinene and

289   β-phellandrene were detected. In the study by Hakola et al. (2003) the MT emission composed mainly of α-pinene, β-

290   pinene, camphene and limonene, but only very small amounts of 3-carene were observed, similarly to the present study.

291   This raises a question whether spruces would have different chemotypes in a similar way as Scots pine has (Bäck et

292   al., 2012).

293   In order to find out how much variability there was between the trees in monoterpene emission pattern, we conducted

294   a study in June in 2014, where we made qualitative analysis from six different spruces growing in a same area (labelled

295   as tree 3 - tree 8). The results for MT emissions are shown in Figure 3. SQT emissions were not significant at that time

296   (about 1 ng g(dw)$^{-1}$ h^{-1}). As expected, the MT emission pattern of the trees was quite different; terpinolene was one

297   of the main MT in the emission of four trees whereas tree 3 emitted only 3% terpinolene. Also limonene and camphene

298   contributions were varying from few percent to about third of the total MT emission. All the measured trees emitted

299   rather similar proportions of α- and β-pinene. The shares of myrcene, β-pinene and 3-carene were low in every tree.

300   Since different MTs react at different rates in the atmosphere (Table 1), the species specific measurements are

301   necessary when evaluating MTs influence on atmospheric chemistry. Currently, air chemistry models very often use

302   only single branch measurements and this can lead to biased results when predicting product and new particle

303 formation. This study and the study of Scots pine emissions by Bäck et al. (2012) show that species specific
304 measurements are necessary, but also that flux measurements are more representative than branch scale emission
305 measurements and averaging over larger spatial scale may be better suited for air chemistry models.

3.4 Standard emission potentials

307 The standard emission potentials were obtained by fitting the measured emission rates to the temperature dependent
308 pool emission algorithm (equation 2) and the light and temperature dependent algorithm (equations 3-5) described in
309 section 2.2). For the temperature dependent algorithm, the nonlinear regression was carried out with two fitted
310 parameters, yielding both the emission potentials and individual β coefficients for each compound group. With the
311 light and temperature dependent algorithm, only emission potentials were obtained. The compounds' emissions fitted
312 using the temperature dependent pool emission algorithm were the ones of the most abundant MT, SQT and the sum
313 of carbonyls for each season, while the analysis with the light and temperature dependent emission algorithm was
314 carried out for isoprene emissions. In the analysis, obvious outliers and other suspicious data were not included. The
315 excluded values typically were the first values obtained right after starting a measurement period, which might still
316 show the effects of handling the sample branch. The isoprene emissions obtained in 2011 were not taken into account
317 in the analysis as they were not properly collected on the cold trap. This was fixed in 2014 and 2015 by changing the
318 adsorbent material. An approach with a hybrid algorithm, where the emission rate is described as a function of two
319 source terms, de novo synthesis emissions and pool emissions, was also tested. However, the results were not
320 conclusive.

321 The standard emission potentials of isoprene, the selected MT and SQT, acetone and C_4-C_6 aldehyde sums are presented
322 in Table 5. Emission potentials are given as spring, early summer, and late summer values. The coefficient of
323 determination (R^2) is also given, even though it is an inadequate measure for the goodness of fit in nonlinear models
324 (e.g. Spiess and Neumeyer, 2010). A more reliable parameter for estimating the goodness of fit is the standard error of
325 the estimate, which is also given.

326 The summertime emission potentials of MT and SQT reflect the typical behaviour of the temperature variability in
327 summer, with low emissions in spring and high emissions in the higher temperatures of late summer. The variability
328 of the emission potential during the growing season and between the individual compounds is large. In late summer
329 limonene and α-pinene had the highest MT emission potentials. SQT exhibit a similar behavior as monoterpene
330 emission potentials with very low springtime and early summer emission potentials while the late summer emission
331 potential is high. In a review by Kesselmeier and Staudt (1999) the reported standard emission potentials (30°C, 1000
332 μmol m^{-2} s^{-1}) of Norway spruces for monoterpenes vary from 0.2 to 7.8 μg g(dry weight)$^{-1}$ h^{-1} and in a study by
333 Bourtsoukidis et al. (2014b) mean emission potential of Norway spruce was 0.89 μg g(dry weight)$^{-1}$ h^{-1} for all data
334 (spring, summer, fall). Our standardized MT emission potentials are lower than earlier reported values being 0.1 μg
335 g(dry weight)$^{-1}$ h^{-1} during late summer, when they were at their highest.

336   This is the first time we have applied fitting the traditional temperature-based emission potential algorithms to

337   measured carbonyl emissions, and based on the spruce emission results, the approach appears to be applicable also on

338   these compounds. The best fit was obtained with the temperature dependent algorithm. The temporal variability of the

339   emission potential was similar to MT- and SQTs. Unfortunately, acetone/propanal and C4-C10 aldehyde measurements

340   were only carried out during the last measurement campaign, but the emission pattern possibly indicates a midsummer

341   maximum, because emissions were clearly identified in June, and already decreasing in late July-August. The isoprene

342   emissions, fitted with the light and temperature emission algorithm, also reflect the light/temperature pattern of

343   summer, with low emissions in spring and high emissions in late summer.

344   In late summer when isoprene emissions were a bit higher the emission model fits the data better and the emission

345   potential for isoprene was 56.5 ng g(dry weight)$^{-1}$h^{-1}. In a review by Kesselmeier and Staudt (1999) the reported

346   standard emission potentials (30°C, 1000 μmol m^{-2} s^{-1}) of isoprene vary from 0.34 to 1.8 μg g(dry weight)$^{-1}$ h^{-1}. Our

347   standardized late summer mean (56.5 ng g(dry weight)$^{-1}$ h^{-1}) is much lower than these earlier reported values.

348   **3.5 Relative reactivity of emissions**

349   In summer in ambient air at this site most of the known OH reactivity (which is ~50 % of the total measured OH

350   reactivity) is coming from the VOCs (Sinha et al. 2010; Nölcher et al. 2012). Other trace gases (NO$_x$, CO, O$_3$, CH$_4$)

351   have a lower contribution. Of these VOCs, aromatic hydrocarbons have only minor contribution compared to the

352   terpenoids (Hakola et al. 2012). In these ambient air studies contribution of SQTs has been much lower than MTs, but

353   those results are misleading, since lifetimes of most SQTs are so short that they can not be detected in ambient air and

354   estimation of their contribution to the local reactivity is possible only directly from the emissions. Here we studied the

355   relative role of different BVOCs to the reactivity of Norway spruce emissions.

356   The relative contribution from each class of compounds to the total calculated OH and O$_3$ reactivity of the emissions

357   *TCRE$_{OH}$* and *TCRE$_{O3}$,* respectively, is depicted in Fig. 3. Nitrate radicals are likely to contribute also significantly to

358   the reactivity, but since the reaction rate coefficients were not available for the essential compounds like β-farnesene,

359   the nitrate radical reactivity is not shown. SQT are very reactive towards ozone and they clearly dominate the ozone

360   reactivity. Isoprene contribution is insignificant all the time towards ozone reactivity, but it contributes 20-30 % of OH

361   reactivity, although the emission rates are quite low. SQT dominate also OH reactivity during late summer due to their

362   high emission rates, but early summer MT contribution is equally important. Contribution of acetone to the *TCRE$_{OH}$*

363   was very small (~0.05% of total reactivity), but reactivity of C$_4$-C$_{10}$ aldehydes was significant, averagely 15% and

364   sometimes over 50% of the *TCRE$_{OH}$*. Of the aldehydes decanal, nonanal and heptanal had the highest contributions. It

365   is also possible to measure total OH reactivity directly and in the total OH reactivity measurements by Nölscher et al.

366   (2013) the contribution of SQTs in Norway spruce emissions also in Hyytiälä was very small (~1%). This is in

367   contradiction to our measurements, where we found very high share of SQTs (75% in late summer). Nölscher et al.

368   (2013) found also very high fraction of missing reactivity (>80%) especially in late summer. Their measurements

369   covered spring, summer and autumn. Emissions of C$_4$-C$_{10}$ aldehydes, which were not studied by Nölscher et al. (2013)

370   could explain part of the missing reactivity.

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4 Conclusions

Norway spruce VOC emissions were measured in campaigns in 2011, 2014 and 2015. Measurements covered altogether 14 spring and summer weeks. The measured compounds included isoprene, MT and SQT and in 2015 also acetone and C_4-C_{10} aldehydes. MT and SQT emission rates were low during spring and early summer. MT emission rates increased to their maximum at the end of June and declined a little in August. A significant change in SQT emissions took place at the end of July, when SQT emissions increased substantially. The seasonality is different from that observed earlier in Germany (Bourtsoukidis et al. 2014b). There Norway spruce emissions (isoprene, MT, SQT) were highest in spring and declined thereafter. The difference in seasonality can be due to different ages of the measured trees (10-15 years in the current study, 80 years in Bourtsoukidis et al. 2014b), different climate or different stress factors. These same factors can also cause lower emission rates measured now in comparison with other studies. The effect of age to the emission potentials should be studied.

In August SQT were the most abundant group in the emission, β-farnesene being the most dominant compound. SQT emissions increased simultaneously with linalool emissions and these emissions were suggested to be initiated due to stress effects. To our knowledge this is the first time when β-farnesene and linalool emissions have been shown to increase simultaneously in natural conditions, although they have been shown to increase in the emissions together due to stress effects. Of the measured compounds, SQTs had highest impact on local O_3 and OH chemistry.This clearly shows the importance of considering also SQTs in atmospheric studies in boreal environment.

Acetone and C_4-C_{10} aldehyde emissions were highest in July, when they were approximately at the same level as MT emissions. C_4-C_{10} aldehydes contributed as much as MT to the OH reactivity during late summer, but early summer only about half of the MT share in early summer. This demonstrates that also emissions of other BVOCs than the traditionally measured terpenoids are important and should be included in atmospheric studies.

The MT emission pattern varies a lot from tree to tree. During one afternoon in June we measured emission pattern of six different trees growing near each other and especially the amounts of terpinolene, camphene and limonene were varying. Due to inconsistent emission pattern the species specific emission fluxes on canopy level should be conducted in addition to the leaf level measurements for more representative measurements. However, only leaf level measurements produce reliable SQT data.

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 Table 1: OH and O3 reaction rate coefficients used in reactivity calculations.

Species	k_{OH} (cm^3 s^{-1})	Reference	k_{O3} (cm^3 s^{-1})	Reference
Isoprene	$2.7 \cdot 10^{-11} \cdot e^{390/T}$	Atkinson et al. (2006)[a]	$1.03 \cdot 10^{-14} \, e^{-1995/T}$	Atkinson et al. (2006)[a]
2-Methyl-3-buten-2-ol	$6.3 \cdot 10^{-11}$	Atkinson et al. (2006)[a]	$1.0 \cdot 10^{-17}$	Atkinson et al. (2006)[a]
α-Pinene	$1.2 \cdot 10^{-11} \cdot e^{440/T}$	Atkinson et al. (2006)[a]	$8.05 \cdot 10^{-16} \cdot e^{-640/T}$	IUPAC[b]
Camphene	$5.33 \cdot 10^{-11}$	Atkinson et al. (1990a)	$6.8 \cdot 10^{-19}$	IUPAC[b]
Sabinene	$1.17 \cdot 10^{-10}$	Atkinson et al. (1990a)	$8.2 \cdot 10^{-17}$	IUPAC[b]
β-Pinene	$1.55 \cdot 10^{-11} \cdot e^{467/T}$	Atkinson and Arey (2003)	$1.35 \cdot 10^{-15} \cdot e^{-1270/T}$	IUPAC[b]
Myrcene	$9.19 \cdot 10^{-12} \cdot e^{1071/T}$	Hites and Turner (2009)	$2.65 \cdot 10^{-15} \cdot e^{-520/T}$	IUPAC[b]
3-Carene	$8.8 \cdot 10^{-11}$	Atkinson and Arey (2003)	$4.8 \cdot 10^{-17}$	IUPAC[b]
p-Cymene	$1.51 \cdot 10^{-11}$	Corchnoy and Atkinson (1990)	$< 5.0 \cdot 10^{-20}$	Atkinson et al. (1990b)
Limonene	$4.2 \cdot 10^{-11} \cdot e^{401/T}$	Gill and Hites (2002)	$2.8 \cdot 10^{-15} \cdot e^{-770/T}$	IUPAC[b]
1,8-Cineol	$1.11 \cdot 10^{-11}$	Corchnoy and Atkinson (1990)	$< 1.5 \cdot 10^{-19}$	Atkinson et al. (1990)
Linalool	$1.59 \cdot 10^{-10}$	Atkinson et al. (1995)	$\geq 3.15 \cdot 10^{-16}$	Grosjean and Grosjean (1998)
Terpinolene	$2.25 \cdot 10^{-10}$	Corchnoy and Atkinson (1990)[a]	$1.6 \cdot 10^{-15}$	IUPAC[b]
Bornylacetate	$1.39 \cdot 10^{-11}$	Coeur et al. (1999)	-	
Longicyclene	$9.35 \cdot 10^{-12}$	AopWin™ v1.92	-	
Isolongifolene	$9.62 \cdot 10^{-11}$	AopWin™ v1.92	$1.0 \cdot 10^{-17}$	IUPAC[b]
β-Caryophyllene	$2.0 \cdot 10^{-10}$	Shu and Atkinson (1995)[a]	$1.2 \cdot 10^{-14}$	IUPAC[b]
β-Farnesene	$1.71 \cdot 10^{-10}$	Kourtchev et al. (2012)	$1.5 \cdot 10^{-12} \cdot e^{-2350/T}$	IUPAC[b]
α-Humulene	$2.9 \cdot 10^{-10}$	Shu and Atkinson (1995)[a]	$1.2 \cdot 10^{-14}$	IUPAC[b]
Alloaromadendrene	$6.25 \cdot 10^{-11}$	AopWin™ v1.92	$1.20 \cdot 10^{-17}$	AopWin™ v1.91
Zingiberene	$2.87 \cdot 10^{-10}$	AopWin™ v1.92	$1.43 \cdot 10^{-15}$	AopWin™ v1.91
Acetone	$8.8 \cdot 10^{-12} \cdot e^{-1320/T} +$ $1.7 \cdot 10^{-14} \cdot e^{423/T}$	Atkinson et al. (2006)[a]	-	
Butanal	$6.0 \cdot 10^{-12} \cdot e^{410/T}$	Atkinson et al. (2006)[a]	-	
Pentanal	$9.9 \cdot 10^{-12} \cdot e^{306/T}$	Thévenet et al. (2000)	-	
Hexanal	$4.2 \cdot 10^{-12} \cdot e^{565/T}$	Jiménez et al. (2007)	-	

Heptanal	$2.96 \cdot 10^{-11}$	Albaladejo et al. (2002)	-
Octanal	$3.2 \cdot 10^{-11}$	AopWin™ v1.92	-
Nonanal	$3.6 \cdot 10^{-11}$	Bowman et al. (2003)	-
Decanal	$3.5 \cdot 10^{-11}$	AopWin™ v1.92	-

577 [a]IUPAC recommendation

578 [b]IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (http://iupac.pole-ether.fr).

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588 **Table 2: Mean temperatures (°C) and rain amounts (mm) during each measurement month in Hyytiälä.**

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	2011		2014		2015	
	temp	rain	temp	rain	temp	rain
April	4.5	17.4				
May	9.3	44.3	9.4	57.4		
June	15.8	65.3	11.8	94.8	11.9	81.5
July			18.6	44.1	14.6	86.7
August					15.2	12.6

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Table 3: Seasonal mean emission rates of isoprene, 2-methylbutenol (MBO), MT, SQT, acetone and C_4-C_{10} carbonyls in ng g(dw)$^{-1}$ h^{-1}. "na" means that the compounds were not included in the analysis. Spring is April-May, early summer 1.6-15.7 and late summer 16.7-31.8. bdl = below detection limit. Values are averages and standard deviations for the three measurement years (2011, 2014, 2015). Other SQT = sum of all other SQTs in emissions. The number of the measurements each season is in parentheses.

	average	stdev	average	stdev	average	stdev
	spring	spring	early summer	early summer	late summer	late summer
isoprene			1.3	3.7	6.0	12
MBO			2.1	4.2	2.4	3.8
Camphene	1.1	1.8	2.9	4.4	3.8	4.1
3-Carene	0.3	0.7	1.1	1.7	0.9	0.6
p-cymene	0.3	0.6	0.9	1.8	0.5	0.5
Limonene	2.7	3.4	6.1	12.2	7.7	9.5
Myrcene	0.2	0.4	1.7	3.7	3.9	5.1
α-Pinene	2.1	3.4	5.8	11.1	9.6	11
β-Pinene	1.0	2.2	1.8	6.2	0.9	1.1
Sabinene	0	0.1	0.5	1.5	0.9	1.6
terpinolene	0	0.2	0.1	0.4	0.3	0.9
bornylacetate	0	0.2	0.5	2.0	1.1	2.1
1,8-Cineol	0.7	0.7	2.1	3.9	1.8	2.2
linalool	na		1.4	2.2	7.9	12
β-caryophyllene	0	0	0.4	2.1	7.2	5.9
β-farnesene	0	0	1.1	4.3	42	29
other SQT	0.1	0.4	1.4	4.7	35	30
Acetone	na		17	11	17	9.0
Butanal	na		2.0	0.7	0.3	0.3
Pentanal	na		4.1	1.1	2.4	0.9
Hexanal	na		5.0	3.0	4.9	2.1
Heptanal	na		5.2	1.2	7.5	2.4
Octanal	na		0.3	0.1	0.4	1.1
Nonanal	na		6.3	2.3	9.9	4.5
Decanal	na		5.6	2.3	7.4	3.8

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605 **Table 4: Average monthly abundances (%) of emitted MTs. T1 (tree1) includes 2011 and T2 2014 and 2015**

606 **measurements. The number of the measurements each month is in parentheses**.

	α-Pinene	Camphene	Sabinene	β-Pinene	Myrcene	Δ³-Carene	p-Cymene	Limonene	Terpinolene
April, T1 (160)	34	19	0	18	1	5	6	18	0
May, T1 (48)	59	9	1	7	1	1	9	10	3
June, T1 (34)	7	25	16	0	34	3	9	4	0
May, T2 (129)	16	11	0	10	5	5	2	51	0
June, T2 (396)	27	15	0	15	5	5	4	29	0
July, T2 (128)	32	15	2	5	7	5	2	27	1
Aug T2 (134)	34	11	3	3	15	3	1	29	1

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611 Table 5: Standard (30 °C) MT, SQT, acetone and C_4-C_{10} aldehyde emission potentials obtained in 2011, 2014 and

612 2015. For isoprene the standard (1000 µmol photons m^{-2} s^{-1}, 30 °C) emission potentials are from the 2015 campaign.

613 The standard emission potential E_S and the β coefficient are given with the standard error of the estimate (StdErr, in

614 parenthesis). R squared and the number of measurements (N, in parenthesis). The fits were made for the spring

615 (April - May), early summer (June – mid July) and late summer (late July – August) periods.

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	Es (StdErr) ng/g(dw)*h	β K-1 (StdErr)	R2 (N)
Spring			
α-pinene	11.6 (0.7)	0.097 (0.006)	0.423 (331)
camphene	2.5 (0.4)	0.045 (0.009)	0.071 (323)
β-pinene	1.9 (0.2)	0.044 (0.007)	0.119 (324)
myrcene	0.6 (0.1)	0.010 (0.011)	0.007 (157)
limonene	5.0 (0.8)	0.032 (0.008)	0.049 (321)
other MT	2.9 (0.2)	0.085 (0.005)	0.433 (329)
β-caryophyllene	0.2 (0.1)	0.018 (0.059)	0.026 (6)
β-farnesene	-	-	- (0)
other SQT	0.7 (0.3)	0.046 (0.029)	0.029 (72)
Early summer			
α-pinene	14.1 (1.0)	0.058 (0.006)	0.145 (489)
camphene	7.0 (0.3)	0.060 (0.004)	0.230 (492)
β-pinene	5.2 (0.6)	0.062 (0.010)	0.076 (426)
myrcene	5.8 (0.3)	0.078 (0.005)	0.326 (356)
limonene	16.7 (0.9)	0.069 (0.005)	0.239 (497)
other MT	7.0 (0.3)	0.074 (0.004)	0.385 (499)
β-caryophyllene	4.8 (1.3)	0.018 (0.019)	0.023 (54)
β-farnesene	6.9 (1.8)	0.012 (0.018)	0.007 (90)
other SQT	6.2 (0.7)	0.055 (0.010)	0.087 (238)
acetone	50.8 (7.2)	0.066 (0.010)	0.362 (71)
aldehydes	59.1 (4.4)	0.043 (0.005)	0.503 (71)
Late summer			
isoprene	56.5 (4.2)		0.473 (70)
α-pinene	39.3 (4.1)	0.153 (0.017)	0.359 (163)
camphene	7.7 (1.2)	0.064 (0.016)	0.094 (161)
β-pinene	2.5 (0.3)	0.075 (0.015)	0.160 (120)
myrcene	21.1 (2.0)	0.191 (0.019)	0.476 (154)
limonene	32.3 (3.6)	0.155 (0.018)	0.336 (163)
other MT	9.9 (1.1)	0.133 (0.016)	0.298 (153)
β-caryophyllene	11.0 (1.2)	0.020 (0.010)	0.032 (129)
β-farnesene	76.9 (7.5)	0.060 (0.010)	0.183 (162)
other SQT	67.3 (8.2)	0.059 (0.013)	0.132 (157)
acetone	31.8 (2.2)	0.061 (0.007)	0.313 (163)
aldehydes	36.8 (3.0)	0.008 (0.007)	0.009 (163)

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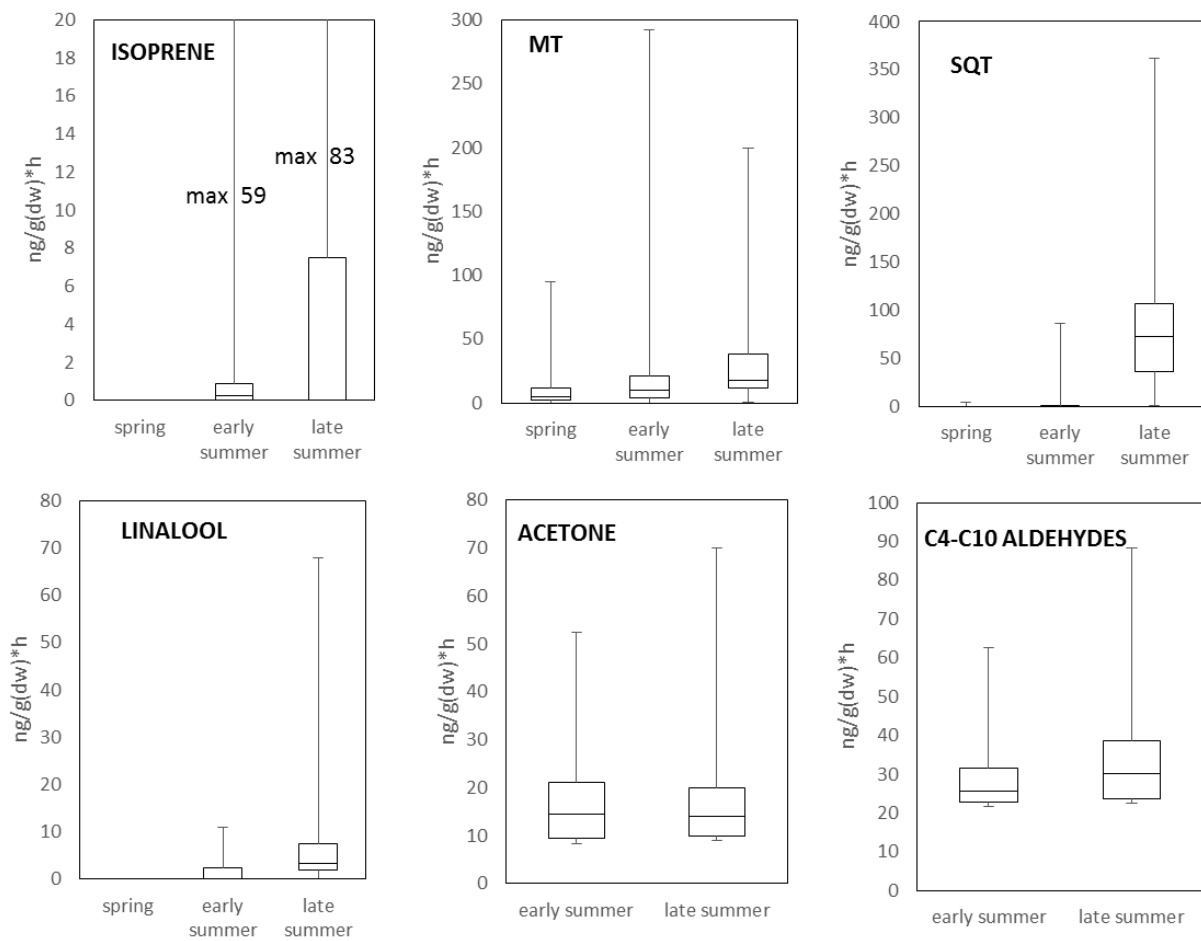
Figure 1: Season mean box and whisker plots of isoprene, MT, SQT, acetone, C4-C10 aldehydes (butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal) and linalool. Boxes represent second and third quartiles and vertical lines in the boxes median values. Whiskers show the highest and the lowest observations.

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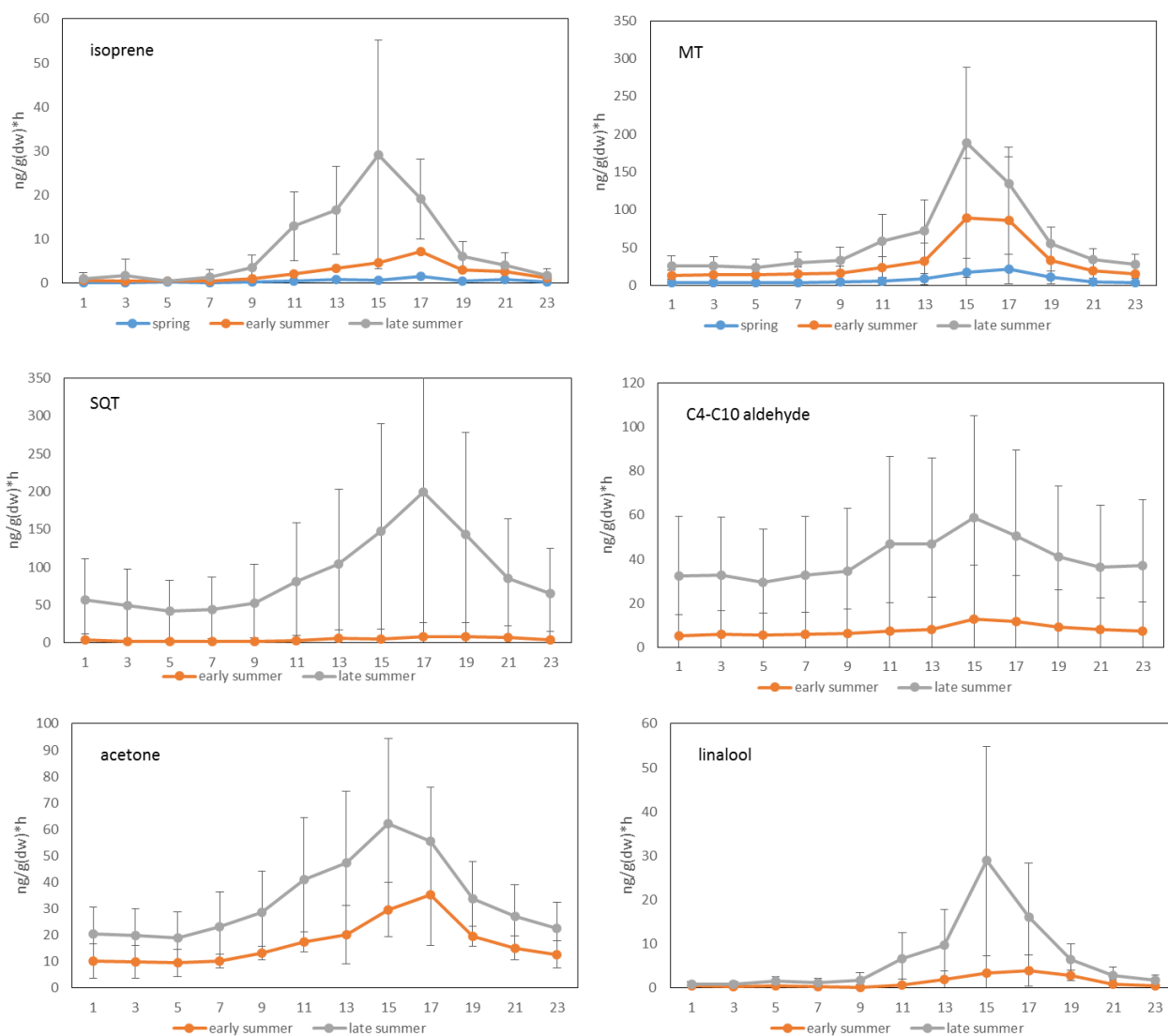
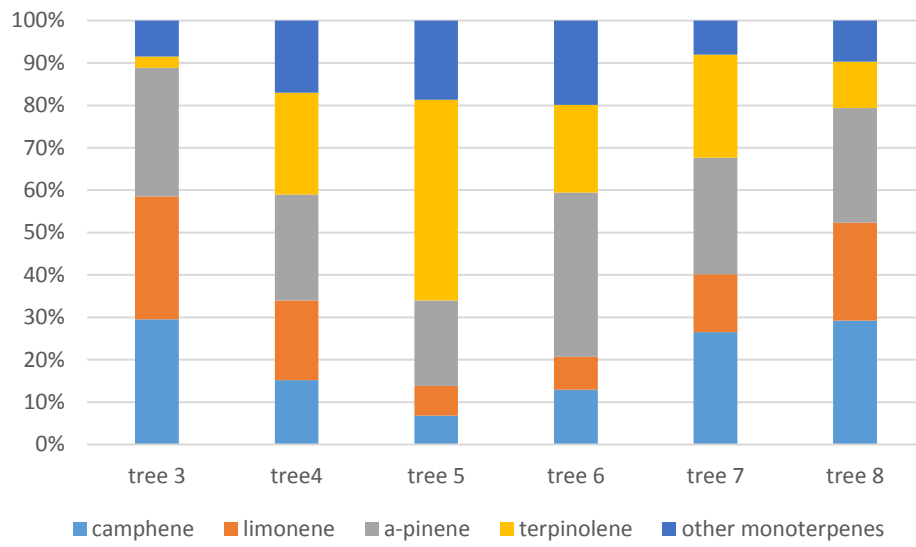


Figure 2: Mean diurnal variations of different compound groups in each season. Spring refers to April and May, early summer June-mid July, late summer mid July-August. Aldehydes are sum of all C$_4$-C$_{10}$ aldehydes (butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal).

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642 **Figure 3: Relative abundances of emitted monoterpenes in six different spruce individuals on 24 June 2014.**
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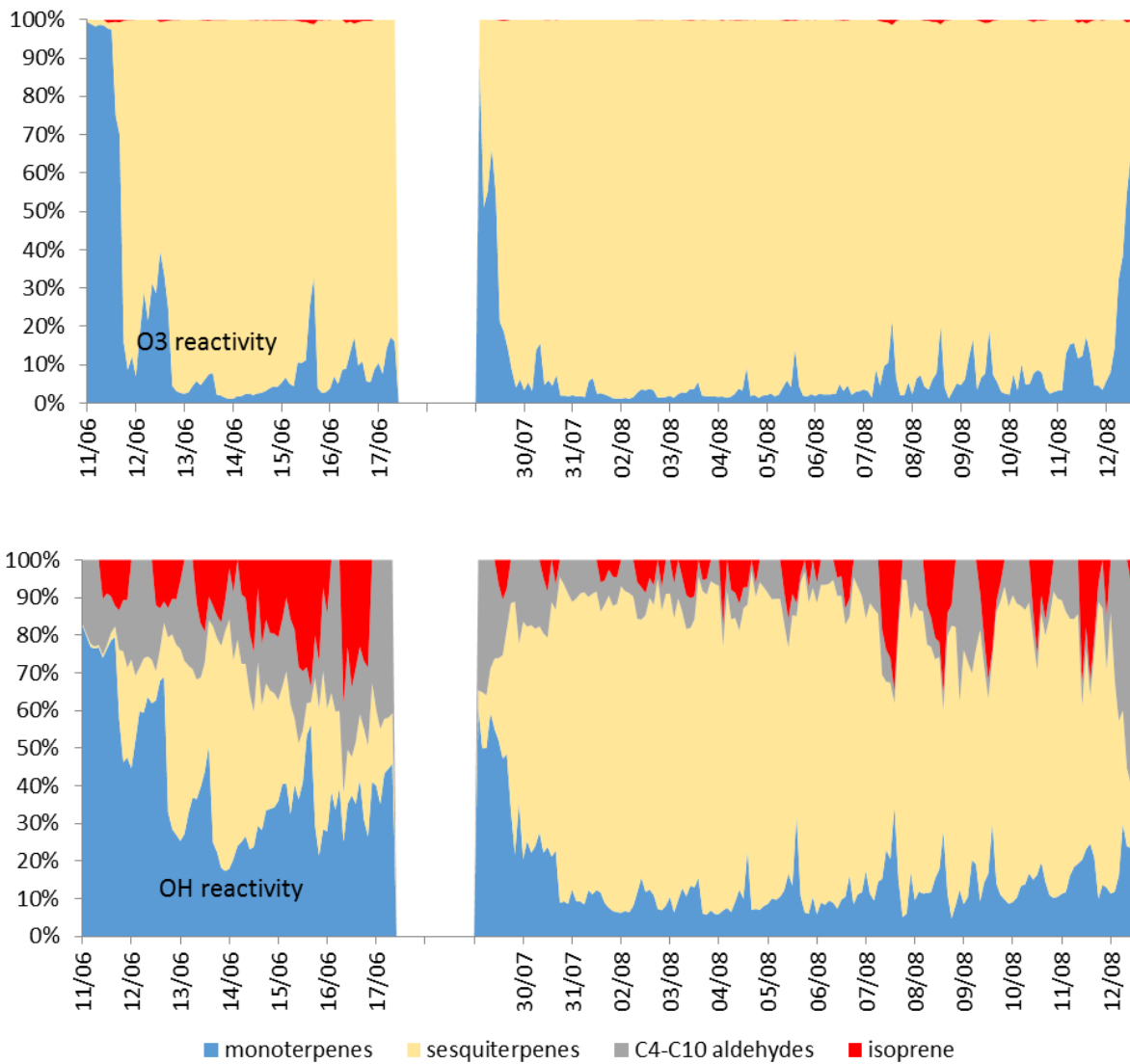
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645 **Figure 4. Relative O₃ and OH reactivity of emissions for two periods in early and late summer 2015. The**
646 **compounds and reaction coefficients used for reactivity calculations are presented in Table 1.**

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