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Terpenoid, acetone and aldehyde emissions from Norway spruce

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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. 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 means 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 84 ng g(dw)$^{-1}$ h^{-1}) concomitant with highest linalool emissions. 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. SQT emissions contributed more than 90 % of the ozone reactivity most of the time, and about 70 % of OH reactivity during late summer. The contribution of aldehydes was comparable to the OH reactivity of MT during late summer, 10 %-30 % most of the time.

1 Introduction

Vegetation produces and emits vast amounts of biogenic volatile organic compounds (VOCs), especially in the densely forested boreal regions (Hakola et al., 2001, 2006; Tarvainen et al., 2005), which are mainly monoterpenes (MT), sesquiterpenes (SQT) and oxygenated volatile organic compounds (OVOCs). In the atmosphere these compounds are oxidized, which affects the tropospheric ozone formation (Chameides et al., 1992) and contribute to the lifetime of methane. In addition reaction products of VOCs also participate in the formation and growth of new particles (Tunved et al., 2006).

In smog chamber studies secondary organic aerosol (SOA) yields for different hydrocarbons and even for different MTs have been found to vary considerably (Griffin et al., 1999). Jaoui et al. (2013) studied SOA formation from SQT and found that the high reactivity of SQT produced generally high conversion into SOA products. Furthermore, they found that the yields were dependent on the oxidant used and were highest for nitrate radical (NO_3) reactions. Of the SQT acidic products, only β-caryophyllinic acid has been observed in ambient samples (Jaoui et al., 2013; Vestenius et al., 2014). Due to their high reactivity, SQT are not usually found in ambient air. Hakola et al. (2012) detected longifolene and isolongifolene in boreal forest air during late summer. Hence, the best way to evaluate the atmospheric impact of SQTs is to measure them from emissions.

In addition to isoprene and MT- and SQTs, plants emit also large amounts of oxygenated compounds i.e. alcohols, carbonyl compounds and organic acids (Koppmann and Wildt, 2007). OVOCs containing six carbon atoms (C_6) are emitted directly by plants often as a result of physical damage (Fall et al., 1999; Hakola et al., 2001). Saturated aldehydes have also been found in direct emissions of plants (Wildt et al., 2003) as well as methanol, acetone and acetaldehyde (Bourtsoukidis et al. 2014b). However, there is very limited amount of data about OVOCs emissions by plants.

In the present study we conducted on-line gas-chromatographic measurements of emissions of MT- and SQTs as well as C_4-C_{10} saturated aliphatic carbonyls from Norway spruce (*Picea abies* L. Karst) branches. Although Norway spruce is one of the main forest tree species in Central and Northern Europe, there are relatively few data on its emissions (Hakola et al., 2003; Grabmer et al., 2006; Bourtsoukidis et al., 2014a and b, Yassaa et al. 2012). In addition to detection of individual MTs gas-chromatograph mass-spectrometer (GC-MS) 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 2012, 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, $61^0 51'$N, $24^0 18'$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).

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 in 2011 was about 10 meters. The samples were collected at a height of about 2 meters from a fully sunlit, healthy lower canopy branch pointing towards a small opening. In 2014 and 2015 a younger tree (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 volume of the cylinder shape transparent Teflon enclosure was approximately 8 litres and it was equipped with inlet and outlet ports and a thermometer inside the enclosure. The photosynthetically active photon flux density (PPFD) was measured just above the enclosure. The flow through the enclosure was kept at about 3-5 litres per minute. Ozone was removed from the ingoing air using MnO_2 coated copper nets. The emission rates were measured using an on-line gas-chromatograph-mass-spectrometer. VOCs from a 40-60 ml/min subsample were collected in 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. This allowed the analysis of MT- and SQTs. 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 sample was collected every other hour. The system was calibrated using liquid standards in methanol injected on Tenax TA-Carbopack B adsorbent tubes. We had no standard for sabinene and therefore it was quantified using the calibration curve of β-pinene. The detection limit was below 1 ppt for all MT- and SQTs. The following compounds were included in the calibration solutions: 2-methyl-3-buten-2-ol (MBO), camphene, 3-carene, p-cymene, 1,8-cineol, limonene, linalool, myrcene, α-pinene, β-pinene, terpinolene, bornylacetate, longicyclene, isolongifolene, β-caryophyllene, aromadendrene, α-humulene, β-farnesene. Isoprene was calibrated using gaseous standard from NPL (National Physical Laboratory). Compared to off-line adsorbent methods this in situ GC-MS had clearly lower background for carbonyl compounds and in 2015 we were able to measure also acetone and C_4-C_{10} aldehyde emission rates. The aldehydes included in the calibration solutions were: butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal. Unfortunately, acetone co-eluted with propanal and the calibration was not linear due to high acetone background in adsorbent tubes used for calibrations.

2.2 Calculation of emission rates

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

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

Here C_2 is the concentration in the outgoing air, C_1 is the concentration in the inlet air, and F is the flow rate into the enclosure. The dry weight of the biomass (m) was determined by drying the needles and shoot from the enclosure at 75 ºC for 24 hours after the last sampling date.

2.3 Emission potentials

A strong dependence of biogenic VOC emissions on temperature has been seen in all emission studies of isoprene, MTs, and SQTs (e.g. Kesselmeier and Staudt 1999; Ciccioli et al. 1999; Hansen and Seufert 2003; Tarvainen et al. 2005; Hakola et al. 2006). The temperature dependent emission rate is usually parameterized as

$$E(T) = E_S \exp(\beta(T - T_S)) \qquad (2)$$

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).

The slope value β is typically obtained from experimental data. Based on literature reviews, the value 0.09 is normally recommended to be used in MT emission modelling (Fehsenfeld et al. 1992; Guenther et al. 1993). In this work we have carried out nonlinear regression analysis with two fitted parameters, arriving at individual slope values for the modelled compounds during each model period. The compounds analysed with the temperature dependent emission rate were the sum of MTs, the sum of SQTs, the sum of aldehydes and acetone.

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 (Guenther et al. 1993). The formulation of the temperature effect is adopted from simulations of the temperature response of enzymatic activity (Guenther et al. 1993). The parameterization for isoprene emissions taking into account both the light and temperature dependence then is

$$E(L,T) = E_S C_L C_T \qquad (3)$$

.

Here *E(L,T)* is the emission rate as a function of photosynthetically active photon flux density *L* (μmol m^{-2} s^{-1}) and leaf temperature *T* (K). E_S is the emission rate at standard conditions of radiation and temperature (usually set at 1000 μmol photons m^{-2} s^{-1} and 30 °C) (Guenther et al. 1993; Kesselmeier and Staudt 1999; Wiedinmyer et al. 2004). C_L and C_T are dimensionless environmental correction factors, accounting for the light and temperature effects on the emissions, with the formulations

$$C_L = \frac{\alpha c_{L1} L}{\sqrt{1+\alpha^2 L^2}} \tag{4}$$

$$C_T = \frac{\exp\frac{c_{T1}(T-T_S)}{RT_S T}}{c_{T3}+\exp\frac{c_{T2}(T-T_M)}{RT_S T}} \tag{5}$$

.

Here R is the universal gas constant (8.314 J K^{-1} mol^{-1}). The factors α (0.0027), c_{L1} (1.066), c_{T1} (95 000 J mol^{-1}), c_{T2} (230 000 J mol^{-1}), c_{T3} (0.961), and T_M (314 K) are empirical constants obtained from experimental data (Guenther et al. 1993; Guenther 1997). In this study a nonlinear regression analysis with the light and temperature dependent emission rate was carried out for the isoprene emissions.

2.4 Chemotype measurements

In order to estimate the between-tree variability there was between the trees, we conducted a study in 2014, where we made qualitative analysis from six different spruces 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. When also the tree that was continuously measured in that day was added to the analysis, we had altogether 7 trees for this qualitative analysis. A branch was enclosed in a Teflon bag and after waiting for 5 minutes we collected a sample on a Tenax tube and analysed later in a laboratory. The samples were taken during one afternoon on 24 June 2014.

2.4 Calculating the reactivity of the emissions

We calculated the total reactivity of the emissions ($TCRE_x$) by combining the emission rates (E_i) with reaction rate co

$$TCRE_x = \sum E_i \, k_{i,x} \tag{6}$$

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

3. Results and discussion

3.1 Weather patterns during the measurements

In 2011, the spring was early and warm. According to the statistics of the Finnish Meteorological Institute the thermal spring started during the first three days of April, with the average temperatures exceptionally high and very little precipitation. The same pattern continued in May, but the weather turned more unstable towards the end of the month, with more rains and cooler night temperatures. The average temperature in June was a little over two degrees higher than normal, and there were some intense thunderstorms. Table 2 shows the mean temperatures and rain amounts during each measurement month.

In 2014, the weather conditions in May were quite typical, with the average temperatures close to the long-term average values. June started with a warm spell, but towards its end the weather was exceptionally cold, and the average temperatures in June were 1 to 2 degrees lower than usual. July was exceptionally warm in the whole country.

In 2015, the June average temperatures were again 1 to 2 degrees below the long-term averages, and there were more rain showers than normally. In July the cold spell and rainy days continued, but in August the warmth returned, with the average temperature 1 to 2 degrees above the long-term average values. August also had exceptionally little rain.

3.2 Variability of the VOC emissions

Since most of the emission rates of the measured compounds were higher in late summer than in early season, we calculated the spring (April and May), early summer (June to mid-July) and late summer (late July and August) mean emissions separately. This described the emission rate changes better than monthly means. Seasonal mean emission rates of isoprene, 2-methyl-3-buten-2-ol (MBO), MT and SQT are presented in Table 3 and typical diurnal variations of the most abundant compounds for each season are shown in Fig. 1.

Norway spruce is known to be a low isoprene emitter and a moderate MT emitter (Kesselmeir and Staudt, 1999; Grabmer et al., 2006; Bourtsoukidis et al., 2014a, b). Our study confirmed these earlier results, although the seasonal pattern of emissions was clearly different. Isoprene emission rates were low early summer, but increased towards August and late summer mean emission rate was 6 ng g(dry weight)$^{-1}$ h^{-1}. The highest daily maxima isoprene emissions were about 70-80 ng g(dw)$^{-1}$ h^{-1}, but usually they remained below 20 ng g(dw)$^{-1}$ h^{-1}. MBO emission rates were even lower than isoprene, the late summer mean was 2.4 ng g(dw)$^{-1}$ h^{-1}. MT emission rates were also low in April, May and still in the beginning of June for 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 increase (about 30 %) to the level where they remained until the end of August, the sum of MT daily maxima still remaining below 300 ng g(dw)$^{-1}$ h^{-1}.

A substantial change in the emission patterns took place at the end of July, when SQT emission rates increased up to 3-4 times higher than the MT emission rates at the same time (Table 3). Such a change in emissions was not observed in a study done in a spruce forest in Germany by Bourtsoukidis et al. (2014b). Instead of late summer increase especially in SQT emissions (in our data from 0 to 84 ng g(dw)$^{-1}$ h^{-1}), they observed highest MT and SQT emissions already during the spring (203 and 119 ng g(dw)$^{-1}$ h^{-1}, respectively) after which emissions significantly declined, median MT emissions being 136 and 80 ng g(dw)$^{-1}$ h^{-1} and SQT emissions 65 and 21 ng g(dw)$^{-1}$ h^{-1} during summer and autumn, respectively. Further, they report that MTs dominated the Norway spruce emissions through the entire measuring period (April-November), SQT emission rates being equal to MT emission rates during spring, but only about half of MT emission rates during summer and about 20 % during autumn. One potential explanation for such a different seasonality may lie in the differences between site specific factors such as soil moisture conditions, local climate, stand age or stress factors. In a boreal forest, late summer normally is the warmest and most humid season favouring high emissions, as was also the case in our study periods. On the contrary, in central Germany July was relatively cold and wet, and according to the authors, reduced emissions were therefore not surprising (Boutsourkidis et al 2014b).

Another interesting feature is shown in the specified emission rates of different compounds. In the current study the main SQT in spruce emissions was β-farnesene. About 50% of the SQT emission consisted of β-farnesene and its maximum emission rate (155 ng $g(dw)^{-1}$ h^{-1}) was measured on the afternoon of 31 July 2015. Two other SQTs also contributed significantly to the total SQT emission rates, but since we did not have standards for these other SQT, their quantification is only tentative. Linalool emissions increased simultaneously with SQT emissions, in the same way as was previously observed in the measurements of Scots pine emissions in the same forest in southern Finland (Hakola et al., 2006), where emissions were found to increase late summer concomitant with the maximum concentration of the airborne pathogen spores, and Hakola et al. (2006) suggested a potential defensive role of the conifer SQT emissions. Several other reports point to similar correlations between SQT (in particular β-farnesene) and oxygenated MTs such as linalool emissions and biotic stresses in controlled experiments. For example, increases in farnesene, methyl salicylate (MeSA) and linalool emissions were reported to be an induced response by Norway spruce seedlings to feeding damage by mite species (Kännaste et al. 2009), indicating that their biosynthesis might prevent the trees from being damaged. Interestingly, the release of (E)-β-farnesene seemed to be mite specific and attractive to pine weevils, whereas linalool and MeSA were deterrents. Blande et al. (2009) discovered pine weevil feeding to clearly induce the emission of MTs and SQTs, particularly linalool and (E)-β-farnesene, from branch tips of Norway spruce seedlings, Also, in a licentiate thesis of Petterson (2007) linalool and β-farnesene were shown to be emitted due to stress. The emissions from Norway spruce increased significantly after trees were treated with methyljasmonate (MeJA). Martin et al (2003) discovered that MeJA triggered increases in the rate of linalool emission more than 100-fold and that of SQTs more than 30-fold. Emissions followed a pronounced diurnal rhythm with the maximum amount released during the light period, suggesting that they are induced de novo after treatment. Our study shows that such major changes in emission patterns can also occur in mature trees in field conditions, and without any clear visible infestations or feeding, indicating that they probably are systemic defence mechanisms rather than direct ones (Eyles et al 2010).

In 2015 we measured also acetone and C_4-C_{10} aldehyde emission rates. The total amount of the measured carbonyl compounds was comparable to the amount of MTs (Table 3) although with our method it was not possible to measure emissions of the most volatile aldehydes, formaldehyde and acetaldehyde, which are also emitted from trees in significant quantities (Cojocariu et al., 2004, Koppmann and Wildt, 2007; Bourtsoukidis et al., 2014b). The carbonyl compounds consisted mainly of acetone (30 %), and the shares of nonanal (21%), decanal (17%), heptanal (14%), hexanal (10%) and pentanal (5%). The shares of butanal and octanal were less than 2% each. Many reports show that the short-chained oxygenated compounds such as aldehydes are effectively released but also absorbed by the vegetation especially when it is moist (e.g. Karl et al., 2005, Seco et al., 2007).

Diurnal variability of the emission rates of MT and SQT, acetone and larger aldehydes are shown in Fig.1. They all show similar temperature dependent variability with maxima during the afternoon and minima in the night. The SQT daily peak emissions were measured two hours later than MT and aldehyde peaks.

3.3 Tree to tree variability in emission pattern

When following the emission seasonality, we discovered that the MT emission patterns were somewhat different between the two trees measured. The tree measured in 2011 (tree 1) emitted mainly α-pinene in May, whereas the tree measured in 2014 and 2015 (tree 2) emitted mainly limonene in May. As summer proceeded the contribution of limonene emission decreased in both trees and the share of α-pinene increased in tree 2. The relative abundance of measured compounds in the spruce emission is presented in Table 4 for all measurement months. The species specific Norway spruce emissions have been measured earlier at least by Hakola et al. (2003) and Bourtsoukidis et al. (2014a). The measurements by Hakola et al. covered all seasons, but only a few days for each season, whereas the measurements by Bourtsoukidis et al. covered three weeks in September-October in an Estonian forest. The main MTs detected in the Estonian forest were α-pinene (59 %) and 3-carene (26 %), but also camphene, limonene, β-pinene and β-phellandrene were measured. In the study by Hakola et al. (2003) the MT emission composed mainly of α-pinene, β-pinene, camphene and limonene, but only very small amounts of 3-carene were observed, similarly to the present study. This raises a question whether spruces would have different chemotypes in a similar way as Scots pine has (Bäck et al., 2012). In order to find out how much variability there was between the trees, we conducted a study in 2014, where we made qualitative analysis from six different spruces growing in a same area (labelled in Fig. 2 as tree 3 - tree 8). When also the tree that was continuously measured in that day was added to the analysis, we had altogether 7 trees for this qualitative analysis. The results for MT emissions are shown in Figure 2. SQT emissions were not significant at that time. As expected, the MT emission pattern of the trees was quite different; terpinolene was one of the main MT in the emission of four trees whereas tree 2 did not emit terpinolene at all and tree 3 only 3 %. Also limonene and camphene contributions were varying from few percent to about third of the total MT emission. All the measured trees emitted rather similar proportions of α- and β-pinene. The shares of myrcene, β-pinene and 3-carene were low in every tree. Since different MTs react at different rates in the atmosphere, the species specific measurements are necessary when evaluating MTs influence on atmospheric chemistry. This study and the study of Scots pine emissions by Bäck et al. (2012) show that species specific measurements are necessary, but also that flux measurements as more representative than branch scale emission measurements and averaging over larger spatial scale may be better suited for air chemistry models.

3.4 Standard emission potentials

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

The standard emission potentials of isoprene, the selected MT and SQT, acetone and C_4-C_6 aldehyde sums are presented in Table 5. Emission potentials are given as spring, early summer, and late summer values. The spring months include April and May, early summer corresponds to June and the first half of July, and late summer to the last half of July and August. The coefficient of determination (R^2) is also given, even though it is an inadequate measure for the goodness of fit in nonlinear models (e.g. Spiess and Neumeyer, 2010). A more reliable parameter for estimating the goodness of fit is the standard error of the estimate, which are also given.

The summertime emission potentials of MT and SQT reflect the typical behaviour of the temperature variability in summer, with low emissions in spring and high emissions in the higher temperatures of late summer. The variability of the emission potential during the growing season and between the individual compounds is large, with lower values in spring and higher in late summer. In late summer limonene and α-pinene had highest emission potentials. SQT exhibit a similar behaviour with very low springtime and early summer emission potentials while the late summer emission potential is high.

This is the first time we have applied fitting the traditional temperature-based emission potential algorithms to measured carbonyl emissions, and based on the spruce emission results, the approach appears to be applicable also on these compounds. The best fit was obtained with the temperature dependent algorithm. The temporal variability of the emission potential was similar to MT- and SQTs. Unfortunately, acetone and aldehyde measurements were only carried out during the last measurement campaign, but the emission pattern possibly indicates a midsummer maximum, because emissions were clearly identified in June, and already decreasing in late July-August. The isoprene emissions, fitted with the light and temperature emission algorithm, also reflect the light/temperature pattern of summer, with low emissions in spring and high emissions in late summer.

In late summer when isoprene emissions were a bit higher the emission model fits the data better and the emission potential for isoprene was 49 ng $g(dw)^{-1}h^{-1}$. Even though the average summertime emission potentials of all studied compounds may well reflect the general warm season emission behaviour, great variability is evident in the monthly or early/late summer results. This variability may reflect e.g. the past temperature history or effects of incident or previous stress events. It should obviously be taken into account when for instance constructing emission inventories for chemical dispersion model applications, because there the reaction potential of some of the emitted compounds may be important in photochemical or particle formation simulations.

3.5 Total reactivity emissions

The relative contribution from each class of compounds to the total calculated reactivity of the emissions $TCRE_{OH}$ and $TCRE_{O3}$ is depicted in Fig. 3. Nitrate radicals are likely to contribute also significantly to the reactivity, but since the reaction rate coefficients were not available for the essential compounds like β-farnesene, the nitrate radical reactivities are not shown. SQT are very reactive towards ozone and they clearly dominate the ozone reactivity. Isoprene contribution is insignificant all the time towards ozone reactivity, but it contributes 20-30 % of OH reactivity, although the emission rates are quite low. SQT dominate also OH reactivity during late summer due to their high emission rates, but early summer MT are equally important. Contribution of acetone to the $TCRE_{OH}$ was very small (~0.05% of total reactivity), but reactivity of C_4-C_{10} aldehydes was significant, averagely 15% and sometimes over 50% of the $TCRE_{OH}$. Of the aldehydes decanal, nonanal and heptanal had the highest contributions. It is also possible to measure total OH reactivity directly and in the total OH reactivity measurements by Nölscher et al. (2013) the contribution of SQTs in Norway spruce emissions also in Hyytiälä was very small (~1%). This is in contradiction to our measurements, where we found very high share of SQTs (75% in late summer). Nölscher et al. (2013) found also very high fraction of missing reactivity (>80%) especially in late summer. Emissions of C_4-C_{10} aldehydes, which were not studied by Nölscher et al. (2013) could explain part of the missing reactivity.

4 Conclusions

Norway spruce VOC emissions were measured in campaigns during 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. In August SQT were the most abundant group in the emission, β-farnesene being the most abundant compound. SQT emissions increased simultaneously with linalool emissions and these emissions were suggested to be initiated due to some stress effects. SQT contributed most to the ozone and OH radical reactivity. Acetone and aldehyde emissions were highest in July, when they were approximately at the same level as MT. 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.

The MT emission pattern varies a lot from tree to tree. During one afternoon in June we measured emission pattern of seven different trees growing near each other; 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, 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	$2.7\cdot10^{-11}\cdot e^{390/T}$	Atkinson et al. (2006)[a]	$1.03\cdot10^{-14}\ e^{-1995/T}$	Atkinson et al. (2006)[a]
2-Methyl-3-buten-2-ol	$6.3\cdot10^{-11}$	Atkinson et al. (2006)[a]	$1.0\cdot10^{-17}$	Atkinson et al. (2006)[a]
α-Pinene	$1.2\cdot10^{-11}\cdot e^{440/T}$	Atkinson et al. (2006)[a]	$8.05\cdot10^{-16}\cdot e^{-640/T}$	IUPAC[b]
Camphene	$5.33\cdot10^{-11}$	Atkinson et al. (1990a)	$6.8\cdot10^{-19}$	IUPAC[b]
Sabinene	$1.17\cdot10^{-10}$	Atkinson et al. (1990a)	$8.2\cdot10^{-17}$	IUPAC[b]
β-Pinene	$1.55\cdot10^{-11}\cdot e^{467/T}$	Atkinson and Arey (2003)	$1.35\cdot10^{-15}\cdot e^{-1270/T}$	IUPAC[b]
Myrcene	$9.19\cdot10^{-12}\cdot e^{1071/T}$	Hites and Turner (2009)	$2.65\cdot10^{-15}\cdot e^{-520/T}$	IUPAC[b]
3-Carene	$8.8\cdot10^{-11}$	Atkinson and Arey (2003)	$4.8\cdot10^{-17}$	IUPAC[b]
p-Cymene	$1.51\cdot10^{-11}$	Corchnoy and Atkinson (1990)	$< 5.0\cdot10^{-20}$	Atkinson et al. (1990b)
Limonene	$4.2\cdot10^{-11}\cdot e^{401/T}$	Gill and Hites (2002)	$2.8\cdot10^{-15}\cdot e^{-770/T}$	IUPAC[b]
1,8-Cineol	$1.11\cdot10^{-11}$	Corchnoy and Atkinson (1990)	$< 1.5\cdot10^{-19}$	Atkinson et al. (1990)
Linalool	$1.59\cdot10^{-10}$	Atkinson et al. (1995)	$\geq 3.15\cdot10^{-16}$	Grosjean and Grosjean (1998)
Terpinolene	$2.25\cdot10^{-10}$	Corchnoy and Atkinson (1990)[a]	$1.6\cdot10^{-15}$	IUPAC[b]
Bornylacetate	$1.39\cdot10^{-11}$	Coeur et al. (1999)	-	
Longicyclene	$9.35\cdot10^{-12}$	AopWin™ v1.92	-	
Isolongifolene	$9.62\cdot10^{-11}$	AopWin™ v1.92	$1.0\cdot10^{-17}$	IUPAC[b]
β-Caryophyllene	$2.0\cdot10^{-10}$	Shu and Atkinson (1995) [a]	$1.2\cdot10^{-14}$	IUPAC[b]
β-Farnesene	$1.71\cdot10^{-10}$	Kourtchev et al. (2012)	$1.5\cdot10^{-12}\cdot e^{-2350/T}$	IUPAC[b]
α-Humulene	$2.9\cdot10^{-10}$	Shu and Atkinson (1995)[a]	$1.2\cdot10^{-14}$	IUPAC[b]
Alloaromadendrene	$6.25\cdot10^{-11}$	AopWin™ v1.92	$1.20\cdot10^{-17}$	AopWin™ v1.91
Zingiberene	$2.87\cdot10^{-10}$	AopWin™ v1.92	$1.43\cdot10^{-15}$	AopWin™ v1.91
Acetone	$8.8\cdot10^{-12}\cdot e^{-1320/T} + 1.7\cdot10^{-14}\cdot e^{423/T}$	Atkinson et al. (2006)[a]	-	
Butanal	$6.0\cdot10^{-12}\cdot e^{410/T}$	Atkinson et al. (2006)[a]	-	
Pentanal	$9.9\cdot10^{-12}\cdot e^{306/T}$	Thévenet et al. (2000)	-	
Hexanal	$4.2\cdot10^{-12}\cdot e^{565/T}$	Jiménez et al. (2007)	-	

Heptanal	$2.96\cdot10^{-11}$	Albaladejo et al. (2002)	-
Octanal	$3.2\cdot10^{-11}$	AopWin^{TM} v1.92	-
Nonanal	$3.6\cdot10^{-11}$	Bowman et al. (2003)	-
Decanal	$3.5\cdot10^{-11}$	AopWin^{TM} v1.92	-

[a] IUPAC recommendation

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

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

	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	18.2	58.5	18.6	44.1	14.6	86.7
August					15.2	12.6

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 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.

	spring (337)	early summer (534)	late summer (159)
Isoprene	bdl	1.3	6.0
MBO	bdl	2.1	2.4
Camphene	1.1	2.9	3.8
3-Carene	0.3	1.1	0.9
p-Cymene	0.3	0.9	0.5
Limonene	2.7	6.1	7.7
Myrcene	0.2	1.7	3.9
α-Pinene	2.1	5.8	9.6
β-Pinene	1.0	1.8	0.9
Sabinene	0.0	0.5	0.9
Terpinolene	0.0	0.1	0.3
Bornylacetate	0.0	0.5	1.1
1,8-Cineol	0.7	2.1	1.8
Linalool	bdl	1.4	7.9
β-Caryophyllene	0.0	0.4	7.2
β-Farnesene	0.0	1.1	42
Other SQT	0.1	1.5	35
Acetone	na	17	17
Butanal	na	2.0	0.3
Pentanal	na	4.1	2.4
Hexanal	na	5.0	4.9
Heptanal	na	5.2	7.5
Octanal	na	0.3	0.4
Nonanal	na	6.3	9.9
Decanal	na	5.6	7.4

Table 4: Average monthly abundances (%) of emitted MTs. T1 (tree1) includes 2011 and T2 2014 and 2015 measurements. The number of the measurements each month is in parentheses.

	α-Pinene	Camphene	Sabinene	β-Pinene	Myrcene	Δ^3-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

Table 5: Standard (30 °C) MT, SQT, acetone and C$_4$-C$_{10}$ aldehyde emission potentials obtained in 2011, 2014 and 2015. For isoprene the standard (1000 µmol photons m^{-2} s^{-1}, 30 °C) emission potentials are from the 2015 campaign. The standard emission potential E_S and the β coefficient are given with the standard error of the estimate (StdErr, in parenthesis). R squared and the number of measurements (N, in parenthesis). The fits were made for the spring (April - May), early summer (June – mid July) and late summer (late July – August) periods.

	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)

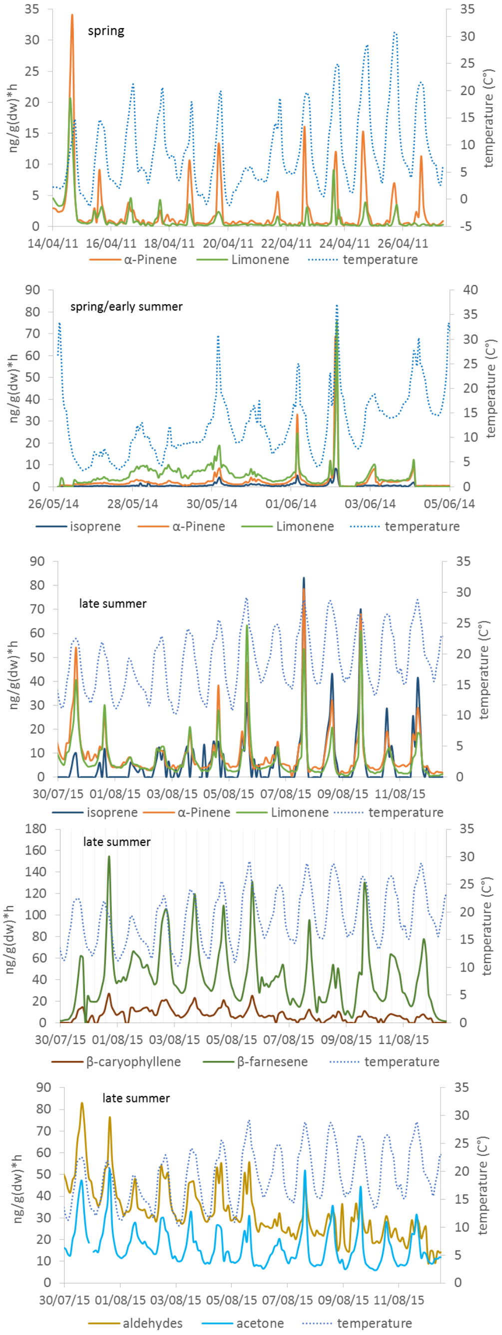

Figure 1: Variability of the most abundant emitted compounds during spring, early and late summer together with enclosure temperature. The most abundant MT were α-pinene and limonene and most abundant SQT β-

caryophyllene and β-farnesene. Aldehydes are sum of all C_4-C_{10} carbonyls (butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal).

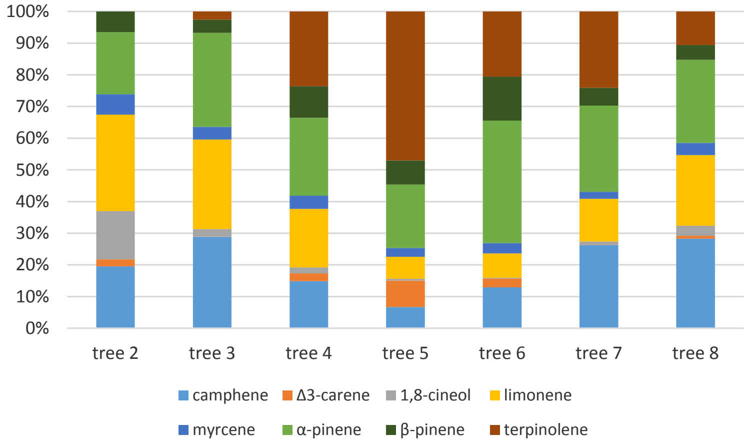

Figure 2: Relative abundances of emitted MTs in seven different spruce individuals on 24 June 2014.

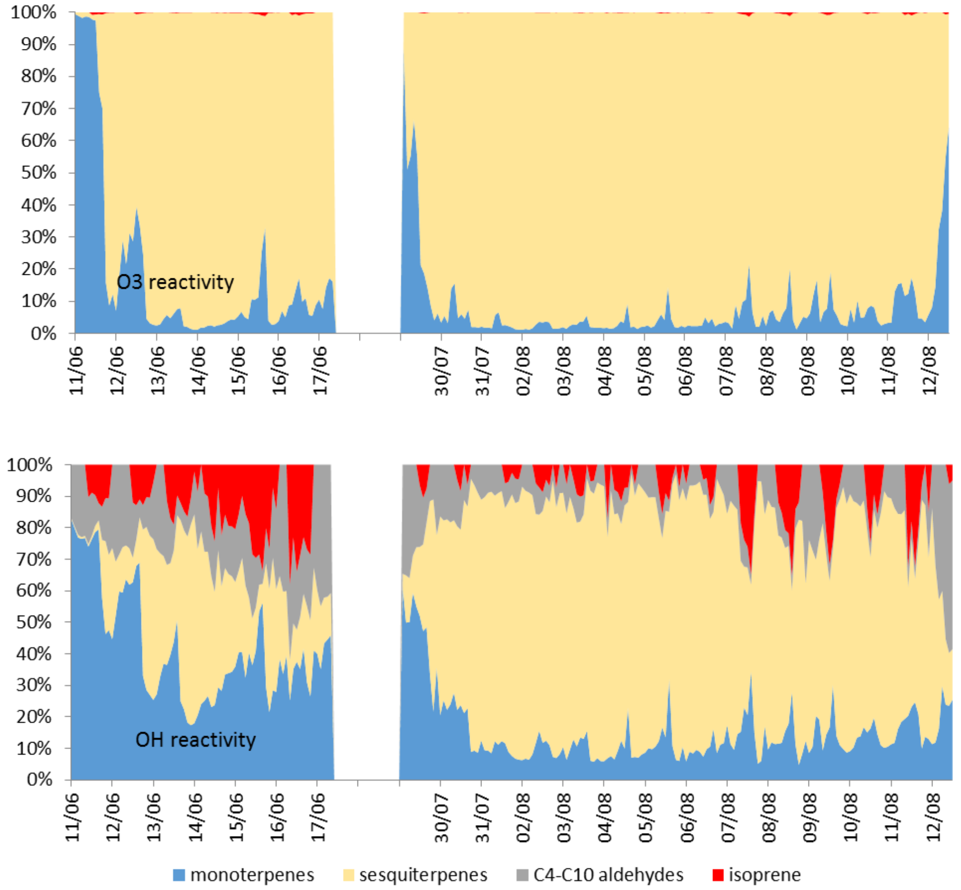

Figure 3. Relative total O_3 and OH reactivity of emissions for two periods in early and late summer 2015. The compounds and reaction coefficients used for reactivity calculations are presented in Table 1.