Author response to "Isoprenoid emission response to changing light conditions of English oak, European beech and Norway spruce"

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We thank the editor and the reviewers for their ideas and suggested improvements of this paper. All suggestions have been carefully considered in order to improve the readability of this manuscript. Below follows a list of changes made according

10 to each referee's suggestions.

Reviewer #1

We thank the reviewer for the thorough review of our manuscript and for the following suggested points of improvement.

Point 1: Some important information in the sample strategy is missing (see also 'specific comments'), but briefly: we would like to understand better why these 3 species were selected? Why this kind of oak? How the two English oaks were selected; the 4 Norway spruces? How 'different' were they... if they were? Were there genetically different? Why 'only' in July?

Thank you for your comment. A main advantage of using the IPG network is that all individuals of the available species used are genetically identical at all of the IPG sites. Each site in the network was initially provided with 2 individuals per species.
For the IPG network garden in Taastrup, we chose to do measurements on English oak, European beech and Norway spruce and we did measurements on all available trees that existed on this site. We chose these three species as they are common European tree species and considered to be high BVOC emitting trees, which we mention on P3 L28. Measurements were only carried out in July as this corresponded to the peak growing season with fully developed leaves and before autumn senescence. This was important to be able to assess responses to the different light levels. Information requested is mentioned in the beginning of the method section (P4 L5-12).

Point 2: Above all, why only the lowest (shaded) branches were sampled? I wonder how a light dependence behavior can be extrapolate from samples taken only from shaded branches, which, by definition, do not adapt very much to light? How could be sure that, some of the surprising discrepancies observed in the results, are not coming from the fact that shaded branches can present quite variable results?

We agree with the reviewer that shaded branches can present quite variable results in terms of emission pattern fluctuations. The decision to only measure the lowest positioned branches of the tree was based on an earlier study (Persson et al., 2016) performed on the same site on the same trees, where the emission patterns at different heights within the canopy were

35 investigated. The results showed little emission pattern difference between the upper and lower canopy levels for the oaks and the spruces, probably due to the relatively wide spacing in between the individual trees, which lets sunlight into the lower canopy as well. The only exception was the beech tree for which there was a clear difference. However, we cannot rule out that there have not been any impacts of the choice of using the lowest branches. This and the

However, we cannot rule out that there have not been any impacts of the choice of using the lowest branches. This and the possibly lower capacity to respond to increasing light availability in the shade-adapted leaves is mentioned in particular regarding the European beech tree the discussion section (P10 L32-33 and P11 L1-9). We also suggest doing more measurements in the upper canopy.

Point 3: What about the weather conditions before the measurements? This can be of importance in the 'story' of the different replicate, and to understand some differences.

Thank you for your comment. We agree that past weather events can influence the emission patterns of the studied tree species. The average weather conditions for July together with the ten-year average are mentioned in the method section (P4

- 5 L13-16). In the discussion section (P11 L23-26) we mention possible effect of drought on the emission patterns, which have been shown to have had an effect on one of the spruces, but we do not mention past weather conditions. We suggest adding a sentence regarding past weather events at P11 L27: "In comparison to the ten-year average weather conditions at the site, July in 2015 has had approximately the same amount of rainfall, but was approximately 2 °C colder. It is likely that the
- weather conditions might have had an effect on the emission results. However, as all trees have had the same exposure it 10 does not fully explain the different responses between trees."

Point 4: In the last part of the MS, additional data from a (another?) 3 year experiment is mentioned: in addition to be not the right place to refer to this(these?) study(ies?), the reader cannot understand why all these date are not merged into one dataset?

In the last part of the manuscript, we are referring to three different experiments which have been performed on the same site, but which have had different study settings and study aims. The results in 2013 was published in Persson et al. 2016, 2014 is unpublished measurement data in which light response were not studied and 2015 data are presented in the present 20 paper. The experiments are therefore not of the same design, but the intention of mentioning them is to point out that the compound composition is not only fairly similar between individuals within the same species, but over different years as well. We suggest rewriting the sentence on P11 L12 to the following: "This emission pattern difference between provenances have been observed for three separate studies performed at the same site (Persson et al. 2016; unpublished data in 2014 and current study in 2015)."

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Point 5: The large discrepancies between the tree replicates is not enough highlighted in the 'results' section, especially for the Early spruce 2 which behaved very differently than other spruce replicates.

Thank you for your comment. We agree that for early spruce the differences in emissions between individuals could be mentioned in the text as well. We will therefore to add the emission values into the text and highlight these. 30

Point 6: Why focusing/structuring the MS on a-pinene, camphene, 3-carene, limonene, eucalyptol? The reason that they were all produced by these species is not enough relevant; let's consider that a non a-pinene emitter were additionally studied, no focus would have been made on this - very - important MT! I'd rather be curious to learn about the total(MT), or the main compound emitted by each species.

As we mention in our manuscript (P8 L27-29), we focus on these particular compounds because we wanted to look at the light responses of common compounds which we know are emitted from different tree species. So we took into consideration not only what compounds we found in our samples, but also which compounds were usually emitted from that

40 particular species. For example we did focus on sabinene as well, even though it was only emitted from European beech. Had it been that we had not had any a-pinene emission from one of the studied species, we would have considered it anyway as it is, as the reviewer points out, a very common and important MT.

We will add a sentence in 3.4 and 4.1 regarding the total MT emission response to light. Our suggestion is as follows (for P7 L15): "The light response for the total MT emission differed between species. Whilst the oaks and the second early spruce 45 showed little or no response to light, the beech and the remaining spruce trees increased their emissions."

For section 4.1, the light responses of MTs are already discussed for oak and beech (P9 L6-7). For spruce we suggest as follows (for P9 L12): "The two provenances of spruce responded differently with an increase in light, where the light dependent fraction of the total MT emission increased for all trees except for early spruce 2. Regarding separate compounds, they were also shown to respond differently with an increase in light depending on the individual tree."

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Point 7: In the 'discussion' section, the MS wobbles constantly between 'compound division point of view' and 'species division point of view': although I do not share the authors belief made for instance page 10 (19-10) of a possible convergence of a light behavior for a same compound for different species (see further specific comments below), the authors has to decide: or they structure their MS on the compound basis or on the species dependency basis.

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Thank you for your comment. As the tree species are quite different in their emission strategies, there are also going to be differences for some compounds in their emission responses. But we could also see that some compounds responded in a similar fashion despite the origin of the compound.

Our suggestion is to make a better species division. P8 L30-31 and P9 L1-5 could be removed from the article and rewritten into the article under the species where they are discussed in order to improve the readability of the text.

Point 8: L27, p4: how the 'anticipated average daily temperature' was obtained?

The anticipated average daily temperature was obtained by weighing in what the weather forecast has predicted for that particular day and based on personal experience regarding the site conditions, with the aim to create as stable and natural conditions as possible within the chamber.

Point 9: Section 3.5 title: could be shorter: 'Photosynthesis and stomatal conductance'

20 Thank you for your suggestion. We will revise the title according to the suggestion of the reviewer.

Point 10: *p8: why p>0.6?*

The p>0.6 refers to an a priori result which is not presented in Table 2, pointing out that there was no statistically significant increase in A_n with an increase in PAR.

Point 11: L18-19 p8 are not at the right place; it could be in the introduction of the discussion.

Thank you for your comment. We agree with this suggestion will move it to the end of the introduction of the discussion section (in old version this would be at P8 L24).

Point 12: L21-24, p8: rather at the end of the introduction/in the presentation of the strategy and objectives.

Thank you for your comment. We agree with this comment and move the sentence to the end of the introduction (P3 L27).

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Point 13: Transition between l29 and l30 p8 is weird.

Thank you for your comment. Since P8 L26-29 is a repetition of the results, we will remove it from the MS to increase its readability.

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Point 14: Don't 'understand l6-7, p9 + the discussion is not on the same level (species effect) than just before (compound effect)

We would argue that the discussion before the mentioned line numbers is a discussion that is both on a species and a compound level. Isoprene and camphene which are mentioned before all had similar responses to light independently of what species it was. Beech is an exception in regards to isoprene as it did not show a capacity to emit that particular compound. Oak and beech was combined in the above mentioned section as they also showed similar responses between species, both in regards to compounds and in regards to species effect. We will revise the manuscript to focus on the species effect in order to make the article a bit clearer.

Point 15: I cannot figure out how a compound is going to be identically controlled by environmental conditions whatever the species. If so, it would make no sense to consider 'de novo' or 'pool' or 'de novo + pool' MT groups (cf. conclusion3-5 p9).

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As we argue a bit further down in the section (P10 L5-12), the results from this study are indicating that there might be similarities in emission responses between species. If that would be the case, it is true that the conception of what should be considered as de novo or pool groups need to be revised. But we are also arguing that the amount of data in this study is generally too low in order to make any robust conclusions. So yes, we can only argue that we saw an indication of similar

emission responses between species, but there is also a need to study it further.

Point 16: L7-9, p9: I don't understand the last part of this sentence.

- The argument of this sentence is that even though there has been an increasing amount of studies showing that de novo 20 species can have non-specific storing capacities (a suggestion is mentioned at P9 L34), there is still a tendency to consider some species as only light dependent or light independent. A suggestion is to rewrite the sentence at P9 L9-11 to the following: "For coniferous tree species, which are known to have storage structures contributing to a considerable lightindependent emission, a division of the emissions into light-dependent and light-independent fractions has been suggested 25 (Ghirardo et al., 2010). Although similar structures are absent in the broadleaf species studied here, the results suggest that
- these species also have a light-independent fraction."

Point 17: L9-11, p9: is a comparison between so different emitters than oak/beech and Norway spruce relevant?

30 It is true that the different emission strategies that exist between the three tree species could make it difficult to find any clear emission pattern similarities. We hope the suggested sentence in point 16 makes the comparison a bit clearer.

Point 18: L12-21 p9 is more a 'result presentation' than a discussion; the early spruce 2 results from Early spruce 2 are indeed different from the other; however the number of samples (n=13) is not that much different from the early spruce 1 (n=14) or oak 1(n=15) and cannot explain all these differences.

Thank you for your comment. We agree that the sample size for spruce 2 is not that much different from the sample sizes for the other studied trees and which is also mentioned on P10 L9-10, P12 L2-3 and P12 L16-17. We suggest to remove the sentence at P9 L12.

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Point 19: Section from line 22 p9 has to been rewritten and better restructured: it starts from the strategy justification, jumps to camphene emission from different emitters (which was also discussed lines 1-5 of the same page 9), then to night emission (thus to the existence of storage structure)...

- 45 We can argue that the new section is not introduced as clearly as it could have been, jumping from individual compounds to discussing de novo and storage capacities. We suggest the following, starting from P9 L22: "Regarding the light dependency of MT emissions, there are several studies which have suggested that both de novo and storage pool emissions can occur within different tree species (Dindorf et al., 2006; Moukhtar et al., 2006; Ghirardo et al., 2010). Our study shows different compounds respond differently ... "We would also suggest to remove unnecessary repetition and to move the first three
- sentences (P9 L22-26) to the end of the section and adapt the first sentence in order to improve the readability. The following 50

is suggested, starting from the last sentence in the section: "These results suggest... de novo emitting tree species need to be considered to have storage pools in emission models as well. However, with the current experimental setup...".

Point 20: Sentence 1 3-5 p10: I don't understand this sentence, since de novo emitting species ARE already considered as 5 having a storage pool in emission models...

Unfortunately we cannot fully understand this point which the reviewer has given. If the reviewer wants to highlight that species can emit both light-dependently and light-independently in models, then that is true and we would rephrase the sentence. But if there is another opinion in the matter, we would need to ask the reviewer to clarify this further.

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Point 21: L5-7 p10: few remarks:

o There is not so 'many' emission models available

o I don't see the link between the growing condition adaptions considered in some emission models and the experimental results presented in this study

o considering a compound division will not improve the plant functional division; it may (?) improve the emission model 15

Thank you for your comments, 'many' can indeed be removed from the manuscript. Regarding the second remark we would argue that the results in this study, where different emission amounts for different light levels are presented, could possibly help to improve the emission algorithms to be more accurate at different light levels. The last remark is correct and the sentence will be rephrased to "improve emission models" instead of "improve the division of plant functional types" (P10

20 L7).

Point 22: L9-10 p10: for decades, studies on BVOC emission variations showed that this 'promising idea' is not a good track to consider: a pinene can be L-dependent for some emitter, but L-independent for other ones: I don't see how this would converge.

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We agree with the reviewer that for some compounds it has been shown that there has been both a light-dependent and lightindependent response depending on which species that has been considered. A-pinene is one of the more well studied compounds, due to its importance in atmospheric reactions and for being a commonly emitted compound by many different species. However, you could also argue that for other compounds, there is less information regarding their response and

which could also have an impact in different types of atmospheric reactions. We suggest to remove the sentence at P10 L9-10

Point 23: section 4.2, p10: I think many results are here clearly presented in this 'discussion' section but should rather be added in the 'results' section which mainly (only?) presents light dependence results and not raw emissions (i.e., the main 35 compounds measured, the ER values, their relative contribution, ...)

We will add the needed information in the results in condensed format and removing them from the discussion section.

Point 24: L22-23, p10: I'm getting confused: were these results obtained over a 3 year study? 40

As was mention in point 4, we are referring to previous measurements done on this same site, but which have had different experimental setups. What we wanted to emphasize is that our results are not only in line with other studies performed elsewhere, but that they are also consistent for the same trees over a number of years. We hope that the suggested revision mentioned in point 4 will correct this matter.

Point 25: L24, p10: I'm not a native English speaker, but I would rather say something like 'the low variation in the emission pattern' rather than 'the low emission pattern variation'

We would argue that the suggested change would refer to only one tree, whilst we want to stress the similarity between all of the trees. Our suggestion is as follows: "This would suggest that even if environmental factors such as temperature or light influence the total emission from oak, these do not alter the compound contribution to a great extent (Staudt et al., 2001; van Meeningen et al., 2016)."

Point 26: L27, p10: why considering now 'total emission' in a discussion section which states earlier that 'looking at emission patterns of separate compound would improve...'; I cannot see the guiding thread of the discussion.

Thank you for your comment. We suggest removing the sentence on P10 L27 and rewriting the sentence at P10 L27 to the following: "There were big differences in emission between beech leaves, making it difficult to see any clear increase in BVOC emission with an increase in light."

Point 27: L28-29 p10: I don't understand: even if some large differences exist between emission rates (ER) from different leaves, a light dependence (or not) can be study for each leave, whatever the absolute values of their emissions

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It is true that the light dependence can be studied for each leaf separately. What we meant with the sentence was that the responses from the leaves were quite different, where some experienced an increase in their emissions with increasing light and where some were decreasing their emissions. We hope the above mentioned sentence in point 26 makes things clearer.

20 Point 28: L 30-31, p10: stress and injury are different things + SQT are not the only compounds related to stress or injury

As we are not focusing on stress or injury in this article, our suggestion is to remove the sentence to make a better flow in the text.

25 Point 29: L33, p10: what is 'the study' carried out in 2013?

The study which we refer to is a study performed in Taastrup in 2013 on this tree, but with a different experimental setup. It is mentioned in the section before (P10 L26), but of which we forgot to refer back to in this section. We will add in the reference into the sentence.

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Point 30: $L1-2 \ p11$: emission rates (ER) and standardized emissions (ER*) are not the same thing; top canopy ER are always 'much higher' than in the shaded canopy ER, but ER* are, or are not different. In this study only ER* were measured (30_, 1000 PAR).

35 We agree that emission rates and standardized emission rates are not the same thing. We suggest to alter the emission rates into standardized emission rates in the sentence.

Point 31: L6-7, p11: I don't understand the sentence

40 Thank you for your comment. A suggestion is to remove the sentence as it is not providing much to the discussion.

Point 32: L13, p11: a mysterious 3 year study is again mentioned; if these additional data are of importance they should be used and presented SINCE the beginning of the manuscript, not at this point of the 'discussion'.

45 As mentioned in point 4 and 25, these are again not part of the same study but different studies with different experimental setups performed at the same trees. We hope the suggestion in point 4 makes the sentence more readable.

Point 33: L18, p11: this conclusion seems incoherent with the points mentioned just before

50 Our suggestion is to remove the sentence.

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Point 34: L19-22, p11: choosing shaded branches makes indeed the light dependency study over a large range of PAR not easy (possible?);

- 5 As the reviewer points out, the response of shade adapted branches is most likely the same as if we would have done our measurements on sun adapted branches. As we point out on P11 L1-4, we have acknowledged that the European beech at this site had different standardized emission rates for the upper and lower parts of the canopy. However, for the remaining trees there was no statistically significant difference between the upper and lower levels, possibly due to wide spacing between trees which provides with light at all canopy levels of the tree. Even though it is uncertain what the response would
- 10 be at the upper canopy, we argued the adaptation at lower levels would still give us reasonable results. Furthermore, we would also argue that the response of the lowest positions branches should not be ignored, even though the response would most likely be quite different at the top of the canopy.

Point 35: Figures 1-3: please use colors rather than grey scales and above all, used the same color (or grey) for each compound in all the figures, otherwise it is quite difficult to follow

Thank you for your comment. We have chosen to have our figures in a grey scale as we did not want the reader to lose any information in case they decide to print the article in black and white. But we agree that for the case of sabinene for European beech and isoprene for English oak, they should be of different colors in order to emphasize that they are different compounds. Our suggestion is to change the color of isoprene to white, in order to be comparable with the Norway spruce

figures and keep the dark grey color for sabinene for the European beech tree.

Point 36: Figure4: choose a color (or grey) for each tree or group of trees; or no color at all, but not only 2 only different greys/colors for 4 different emitters

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We will change the bars to be uniform in color.

Point 37: I would not mind if the Appendice were a Table; in any case its presentation should be improved (e.g.: it is hard to understand which values correspond to which category '0' and '500' for oak 1...)

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We agree that the readability of the table can be improved, which we will change with the update of the manuscript.

Reviewer #2

We thank the reviewer for the thorough review of our manuscript and for the following suggested points of improvement.

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Point 1: In Fig. 3: For early spruce 2, the emission rates of isoprene and total MT were extremely low at 1000 µmol m-2s-1, please give an explanation.

We were also surprised over the extremely low emission levels for early spruce 2 and can unfortunately not give any conclusive explanations. We believe though that the underlying reasons are most likely relatively high variation between samples, few samples to begin with and that the tree might not be fully recovered from a drought stress event which happened in 2013 (mentioned on P9 L16-18 and P11 L22-29).

On behalf of all authors,

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Ylva van Meeningen

Isoprenoid emission response to changing light conditions of English oak, European beech and Norway spruce – List of relevant changes

- Introduction An additional sentence in the end of the section, which has been moved from the discussion section
- Results Additional emission values added and the 3.5 headline has been shortened
 - **Discussion** Values have been moved to the result, the sections have been revised and divided further into species, a few sentences on weather has been added
 - Appendix Has been divided into three sections instead of one
 - Figures Fig. 01 color for isoprene has been changed and Fig. 04 has a uniform colour

Isoprenoid emission response to changing light conditions of English oak, European beech and Norway spruce

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- 10 Abstract. Light is an important environmental factor controlling biogenic volatile organic compound (BVOC) emissions, but in natural conditions its impact is hard to separate from other influential factors such as temperature. We studied the light response of foliar BVOC emissions, photosynthesis and stomatal conductance on three common European tree species, namely English oak (*Quercus robur*), European beech (*Fagus sylvatica*) and two provenances of Norway spruce (*Picea abies*) in Taastrup, Denmark. Leaf scale measurements were performed on the lowest positioned branches of the tree in July
- 15 2015. Light intensity was increased in four steps (0, 500, 1000 and 1500 μ mol m⁻² s⁻¹), whilst other chamber conditions such as temperature, humidity and CO₂ levels were fixed.

Whereas the emission rate differed between individuals of the same species, the relative contributions of compounds to the total isoprenoid emission remained similar. Whilst some compounds were species specific, the compounds α -pinene, camphene, 3-carene, limonene and eucalyptol were emitted by all of the measured tree species. Some compounds, like

- 20 isoprene and sabinene, showed an increasing emission response with increasing light intensity, whereas other compounds, like camphene, had no significant emission response to light for most of the measured trees. English oak and European beech showed high light-dependent emission fractions from isoprene and sabinene, but other emitted compounds were light-independent. For the two provenances of Norway spruce, the compounds α-pinene, 3-carene and eucalyptol showed high light-dependent fractions for many of the measured trees. This study highlights differences between compound emissions in
- 25 their response to a change in light and a possible light independence for certain compounds, which might be valid for a wider range of tree species. This information could be of importance when improving emission models and to further emphasize the discussion regarding light or temperature dependencies for individual compounds across species.

1 Introduction

Biogenic volatile organic compounds (BVOCs) are produced in both marine and terrestrial environments, playing important roles in both plant survival and in the reactive chemistry of the atmosphere (Guenther et al., 1995; Goldstein and Galbally, 2007). Isoprenoids, such as isoprene (a C_5 unit), monoterpenes (MTs, consisting of two C_5 units) and sesquiterpenes (SQTs,

- 5 consisting of three C_5 units) contribute with approximately 68% of the total global BVOC emissions (Guenther et al., 2012). They are some of the most important BVOC groups due to their high volatility and involvement in several atmospheric reactions (Atkinson and Arey, 2003; Goldstein and Galbally, 2007, Guenther et al., 2012). The degradation of BVOCs in the air influences atmospheric processes such as production and destruction of ozone (Atkinson, 2000; Peñuelas and Staudt, 2010), but it also influences the growth of secondary organic aerosols (SOA) (Claeys et al., 2004; Ehn et al., 2014). SOA
- 10 particles are known to scatter incoming solar radiation and to act as cloud condensation nuclei, which in turn have an effect on the incoming and outgoing radiation (Laothawornkitkul et al., 2009 and references therein; Paasonen et al., 2013). In general, SOA yields are expected to be higher for compounds with internal double bonds, such as α-pinene, 3-carene, limonene and terpinolenes. However, some acyclic compounds, such as myrcene, have also been observed to produce high SOA yields (Lee et al., 2006 and references therein).
- 15 The production and release of BVOCs are sensitive to physical constraints such as light and temperature (Staudt and Bertin, 1998; Niinemets et al., 2004; Dudareva et al., 2006). Temperature controls the synthesis of isoprenoids and the diffusion rate of compounds (Niinemets et al., 2004 and references therein). The light availability determines the amount of isoprenoid precursors produced by photosynthesis and the available amount of ATP and NADPH, which are used in the CO₂ fixation and assimilation reactions that provide new isoprenoids (Niinemets et al., 2004 and references therein; Lichtenthaler, 2007).
- 20 However, the emission rates can also be affected by physiochemical constraints, such as stomatal conductance (G_S). G_S can control VOC emissions temporarily in a non-steady state, when the intercellular volatile partial pressure is different from the equilibrium pressure (Niinemets and Reichstein, 2003). In a steady state, isoprene and MTs are insensitive to stomatal closure because of their high gas-phase to liquid-phase partitioning. Compounds with a large Henry's law constant (H), such as isoprene and MTs, partition to the gas phase, whilst low H compounds partition to the aqueous phase. When G_S decreases,
- 25 it elevates the gas-phase partial pressure inside the stomata and increases the gradient between the intercellular air-space and atmosphere. This allows the diffusion flux of compounds with a high H to be maintained independently of stomatal conductance (Niinemets and Reichstein, 2003; Niinemets et al., 2004).

Isoprene is released upon production and therefore shows a strong direct temperature and light dependency (Kesselmeier and Staudt, 1999; Niinemets et al., 2004). The light dependency of MT emissions has, however, been more debated. In earlier

30 studies regarding MT emissions, a lack of light response led to the assumption that MTs were only temperature dependent (Tingey et al., 1980). Emissions of MTs were assumed to originate from internal storage structures in plants, such as resin ducts, oil glands or glandular hairs and trichomes (Fuentes et al., 1996; Kesselmeier and Staudt, 1999). The evaporation from these structures is controlled by the vapour pressure of the MTs, which in turn is affected by the air temperature and concentration of MTs within these structures (Lerdau et al., 1997; Ghirardo et al., 2010; Taipale et al., 2011). However, more recent studies have suggested that both *de novo* and storage pool emissions can occur simultaneously. Amongst MT emitting broadleaved trees, such as Holm oak (*Quercus ilex*) and European beech (*Fagus sylvatica*), it was recognised that MT emissions were predominantly controlled by light-dependent mechanisms (Staudt and Seifert, 1995; Tollsten and Müller,

5 1996; Dindorf et al., 2006). Later on, coniferous trees were also recognized to potentially emit part of their total emission as *de novo* emissions (Shao et al., 2001; Tarvainen et al., 2005; Moukhtar et al., 2006; Ghirardo et al., 2010; Taipale et al., 2011).

Shao et al. (2001) measured the BVOC emissions from Scots pine (*Pinus sylvestris*) in darkness and in different light conditions. They found that MT emissions were partly influenced by photosynthetically active radiation (PAR), indicating

- 10 that observed emissions originate both from storage pools and from direct biosynthesis. Ghirardo et al. (2010) used stable isotope labelling on Norway spruce (*Picea abies*) and Scots pine and observed that the approximate contribution of *de novo* MT emissions could range between 25 and 45% for spruce and 40 and 70% for pine. Since it has been shown that light-dependent and light-independent emissions happen simultaneously, it has been suggested that the observed MT emission patterns should be regarded as a combination of light-dependent and light-independent emissions instead of only being light-
- 15 independent for some species (Ghirardo et al., 2010; Taipale et al., 2011; Laffineur et al., 2011; Staudt and Lhoutellier, 2011; Song et al., 2014).

Many emission models face the difficulty of generalizing a species or class of species into one emission potential, despite of different growing conditions and emission variabilities within species. Even though the BVOC emission patterns tend to be more similar for plants of the same species or genus, variations in emission rates have been observed. Staudt et al. (2001)

- 20 screened 146 individual holm oak trees, which could be distinguished into three main types with an almost stable BVOC composition. Their results suggest that the observed emission composition is more related to genotypic differences than to environmental impacts. Bäck et al. (2012) sampled branches from 40 mature Scots pine trees from adjacent pine stands. They could divide the trees into three chemotypes which remained fairly stable with the progression of the season. The importance of genetic diversity on observed emission patterns has been further emphasized by Persson et al. (2016) who
- 25 investigated the emission patterns in genetically identical trees of English oak (*Quercus robur*), European beech and Norway spruce. Persson et al. (2016) found differences in compound composition between two provenances of spruce, but little emission pattern differences for the remaining trees of identical genotypes. However, f Few studies have investigated in situ if the compounds emitted from different tree species respond similarly with a conditional change in light. Our aim was to investigate how different compounds responded to changing light conditions and if the response was similar between
- 30 different tree species.

In this study, we investigated the response of BVOC emission, photosynthetic rates and stomatal conductance of English oak, European beech and Norway spruce to different light levels. These species were chosen as they are some of the most common tree species growing in large areas within Europe (Skjøth et al., 2008) and have reported BVOC emission levels exceeding >1 μ g gdw⁻¹ h⁻¹ (Kesselmeier et al., 1999; Dindorf et al., 2006; Holzke et al., 2006; Pokorska et al., 2012). The

study aims to: (i) analyse how emissions of different BVOCs respond to changing light levels, to identify light-dependent fractions for each compound; and (ii) investigate if there are similar patterns between observed BVOC emission, photosynthetic rates and stomatal conductance. This information could be useful for our understanding of how the emission patterns of common European tree species react to changing light, which could possibly improve the algorithms used in emission models.

2 Methods

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2.1 Site description and plant material

Measurements were carried out 10-31 July in 2015 at the International Phenological Garden (IPG) site Taastrup, Denmark (55°40'N, 14°30'E), maintained by the Faculty of Science at the University of Copenhagen. The IPG network performs 10 long-term phenological observations at several sites throughout Europe on some of the most common European plant species. Each site was initially provided with up to two individuals per species. The plants used in the network are

- genetically identical clones, which means the genetic variation between individuals and sites is absent (Chmielewski et al., 2013). At the IPG network site at Taastrup, there are 21 trees from 13 different species and provenances with one or two individuals per species. All trees presented here were planted in 1971. Measurements were performed on two English oaks,
- 15 one European beech and four Norway spruces, the latter divided into two provenances according to the framework of IPG. These provenances differ in their budburst patterns; one provenance has a budburst approximately one week earlier than the other. These provenances of spruce will henceforth be referred to as early spruce and late spruce.

During the measurement period, the weather was quite cold and humid, with an average daily temperature ranging between 13.1 and 18.8 °C and with a total rainfall of 43.6 mm during the three weeks of measurements. The average temperature and total rainfall for July 2015 was 16.4 °C and 75 mm whilst the ten-year (2006-2015) average temperature and rainfall in the

area was approximately 18.2 °C and 71.8 mm (dmi.dk).

2.2 BVOC measurements at different light levels

Between 13 and 21 samples were taken from each tree. All measurements were made on the lowest positioned branches (1-2 m above ground) and on the southwest or south facing side of the tree using a portable photosynthesis system (Li-6400 XT,

- 25 LICOR, NE, USA) equipped either with a LED source leaf chamber (6400-02B) for deciduous trees or a lighted conifer chamber (6400-22L) for the coniferous trees. The ingoing air stream (700 ml min⁻¹) into the chambers passed through a hydrocarbon trap and O₃ filter to remove organic contaminants and ozone in order to avoid BVOC oxidation before sampling. Measurements were performed during daytime (8:00-16:00). The calculations of net assimilation rates (A_n) and G_s were performed by the instrument software, using the equations presented by von Caemmerer and Farquhar (1981). All
- 30 measurements were made under fixed environmental conditions. Each leaf or needle twig was acclimated to 400 μ mol CO₂ mol⁻¹ air and 50-60% relative humidity for one hour before BVOC emission sampling. The temperature within the chamber

was set according to the anticipated average daily temperature (18-23 °C during the campaign) in order to minimize potential stress emissions from the plant. Each leaf or needle twig was measured under four light levels (0, 500, 1000 and 1500 μ mol m⁻² s⁻¹) by stepwise increasing PAR from 0 μ mol m⁻² s⁻¹ to 1500 μ mol m⁻² s⁻¹. This direction was chosen in order to mimic the daily increase in light intensity. After the first acclimation period of one hour at 0 μ mol m⁻² s⁻¹, an additional 30-minute acclimation period was applied after switching to a new light level in order to ensure that the leaf or needle twig had adjusted to the new conditions. This acclimation time was chosen based on preliminary tests showing that leaf photosynthesis remained reasonably stable after 30 minutes' adjustment to the new light intensity. The BVOC emissions from the trees were collected by extracting air from the chamber outlets into stainless steel cartridges (Markes International Limited, Llantrisant,

10 extraction was performed using flow-controlled pocket pumps (SKC Ltd., Dorset, UK) with a flow rate of 200 ml min⁻¹. Empty chamber blanks were collected every second day with the same chamber conditions in order to account for possible background contamination in the measured samples.

UK) packed with adsorbents Tenax TA (a porous organic polymer) and Carbograph 1TD (graphitized carbon black). The air

2.3 BVOC analysis

- The BVOC sample cartridges were sealed with Teflon coated brass caps directly after sampling, stored at 3 °C and analysed 15 within eight weeks. A gas chromatograph-mass spectrometer (7890A Series GC coupled with a 5975C inert MSD/DS Performance Turbo EI system, Agilent, Santa Clara, CA, USA) was used for analysis after thermal desorption (UNITY2 coupled with an ULTRA autosampler, Markes, Llantrisant, UK). The oven temperature was held at 40 °C for 1 min, raised to 210 °C in steps of 5 °C min⁻¹ and lastly up to 250 °C in steps of 20 °C min⁻¹. Helium was used as the carrier gas and the BVOC separation was done with a HP-5 capillary column (50 m, diameter 0.2 mm and film thickness 0.33 μm). The
- 20 identification and quantification of BVOCs was done using pure standard solutions for isoprene, α-pinene, camphene, β-pinene, δ-phellandrene, ρ-cymene, 1,8-cineole, ocimene, γ-terpinene, terpinolene, linalool, aromadendrene, α-humulene and nerolidol in methanol (Fluka, Buchs, Switzerland). These standard solutions were injected into adsorbent cartridges in a stream of helium. If there was a compound detected without an available standard, it was identified according to the mass spectra in the NIST library, and quantified using α-pinene for MTs and α-humulene for SQTs. The sample chromatograms
- 25 were analysed with the MSD Chemstation Data Analysis software (G1701CA C.00.00 21 Dec 1999; Agilent Technologies, Santa Clara, CA, USA). Compounds that were found in the empty chamber blanks collected in the field were subtracted from the samples. Only isoprenoids were analysed in this study. Emissions were calculated by using the emission rate equation for the dynamic enclosure technique presented by Ortega and Helmig (2008). For each of the three light levels above 0, the light-dependent fraction of the total compound emission was calculated [as 100% × (light emission - dark
- 30 emission)/light emission] and used as an indicator for its emission response to changing light. The values ranged from 0% (no light-dependence) to 100% (compound emitted entirely light-dependently).

2.4 Statistical analysis

Repeated measures ANOVA tests were computed in the Rstudio software (Rstudio team, 2015, version 0.99.491) in order to test if the observed emission rates of each compound and the A_n or G_S rates differed statistically between the light levels. If a significant effect of light was observed, a simple a priori contrast was used to test which light level was significantly different from the dark measurements. The statistical analyses were done separately for each tree species.

3 Results

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3.1 BVOC emission from English oak

Figure 1 shows the total BVOC emission rate and the compound contributions of the two English oaks at different light levels. The English oak clones in this study had emission rates between $3.5-18.3 \ \mu g \ dw^{-1} \ h^{-1}$ at a light level of 1000 μ mol m⁻¹

- $\frac{2 \text{ s}^{-1} \text{ and a set temperature range of 18-21 °C.}}{\text{ light levels, whilst the emission rate of the second oak saturated at 1000 µmol m⁻² s⁻¹, <u>The English oak clones in this study</u> had emission rates between 3.5 18.3 µg gdw⁻⁴ h⁻⁴ at a light level of 1000 µmol m⁻² s⁻¹, <u>The English oak clones in this study</u> had emission rates between 3.5 18.3 µg gdw⁻⁴ h⁻⁴ at a light level of 1000 µmol m⁻² s⁻⁴ and a set temperature range of 18.21 <u>°C.</u> These emission rates are in line with the standardized emission rates reported by previous studies (Isidorov et al., 1985; Kesselmeier and Staudt, 1999; Pokorska et al., 2012; Persson et al., 2016)₇. (Table 1). Between one and seven compounds$
- 15 were detected at the measured light levels and the detected compounds were isoprene, tricyclene, α -pinene, camphene, 3carene, limonene and eucalyptol. The main emitted compound was isoprene, with no emission during darkness and an emission rate between 2.3-19.8 µg gdw⁻¹ h⁻¹ for oak 1 and 1.3-9.3 µg gdw⁻¹ h⁻¹ for oak 2 at light levels of 500-1500 µmol m⁻² s⁻¹. The relative contribution of isoprene to the total emission with light levels at or above 500 µmol m⁻² s⁻¹ was >96% (Fig. 1). At a light level of 0 µmol m⁻² s⁻¹, the main detected compounds were limonene and α -pinene. The emissions of these MTs
- 20 remained stable across measured PAR levels, with emission rates of $<0.1 \ \mu g \ gdw^{-1} \ h^{-1}$ at all levels (see Appendix A for absolute values).

3.2 BVOC emission from European beech

In contrast to English oak, European beech showed a smaller and non-significant response of the total isoprenoid emission rate to a change in light (Table 1, Fig. 2). Beech emitted between one and five detected isoprenoids in darkness and between four and eight with light. Detected compounds were tricyclene, α -pinene, camphene, sabinene, 3-carene, limonene,

25 four and eight with light. Detected compounds were tricyclene, α -pinene, camphene, sabinene, 3-carene, limonene, eucalyptol and caryophyllene. Sabinene was not detected at 0 µmol m⁻² s⁻¹ but was the main emitted compound with light, increasing from 66% of the total emission at 500 µmol m⁻² s⁻¹ to 76% at 1500 µmol m⁻² s⁻¹. Limonene was the main emitted compound in darkness. The amount of limonene released remained fairly stable across the studied light levels and ranged between 0.06 and 0.09 µg gdw⁻¹ h⁻¹. The other emitted MTs did not change their emission patterns with increasing light. At

light levels 1000 and 1500 μ mol m⁻² s⁻¹, the SQT caryophyllene was released, with the highest emissions at 1500 μ g gdw⁻¹ h⁻¹ (see Appendix A for absolute values, Fig. 2).

3.3 BVOC emission from Norway spruce

Figures 3a and b show the emission rate and the compound contribution with increasing light levels for early spruce and late 5 spruce, respectively. All four spruce trees emitted isoprene with light (P<0.001 for early spruce 1 and late spruce 1 and 2, P>0.1 for early spruce 2) with a contribution to the total emission of 30-65%. In contrast, limonene and α -pinene were emitted both in darkness as well as with light, but with lower absolute emissions in darkness (see Appendix A for absolute values, Fig. 3). Early spruce 1 had an emission rate of 0.5-0.6 µg gdw⁻¹ h⁻¹, whilst early spruce 2 ranged between 0.1-0.4 µg gdw⁻¹ h⁻¹ with light. For early spruce, bBetween four and nine isoprenoids were detected, which, - These-were isoprene,

- 10 tricyclene, α-pinene, camphene, β-pinene, 3-carene, limonene, eucalyptol, linalool, α-farnesene and β-farnesene. Only one of the two early spruce trees emitted linalool and SQTs. The main detected compound for both trees was isoprene, followed by limonene. The total emission from early spruce 1 saturated at 500 µmol m⁻² s⁻¹ with no significant change with increasing light (P>0.1), whilst early spruce 2 decreased its total emission to 0.1 µg gdw⁻¹ h⁻¹ at 1000 µmol m⁻² s⁻¹ and then increased again somewhat at to 0.3 µg gdw⁻¹ h⁻¹ at 1500 µmol m⁻² s⁻¹ (Fig. 3a). Late spruce emitted two to ten isoprenoids at all light
- 15 levels and the detected compounds were isoprene, tricyclene, α -pinene, camphene, β -pinene, 3-carene, α -terpinene, limonene, eucalyptol and γ -terpinene. β -pinene was emitted by both provenances of Norway spruce, but with higher emissions rates from late spruce in combination with higher emissions of α -pinene. Only late spruce 1 emitted tricyclene and α -terpinene and only at PAR levels of 1000 and 1500 µmol m⁻² s⁻¹. Both trees had an increase in total emission up to 1000 µmol m⁻² s⁻¹, with a decrease in emissions at 1500 µmol m⁻² s⁻¹ for late spruce 1. Late spruce 1 reached its peak emission of
- 20 $2.2 \ \mu g \ g \ dw^{-1} \ h^{-1} \ at \ 1000 \ \mu mol \ m^{-2} \ s^{-1}$, whilst late spruce 2 had a stable emission between 0.6-0.9 $\ \mu g \ g \ dw^{-1} \ h^{-1}$ with light. The emitted compounds from late spruce 1 followed a similar emission pattern as the total emission rate, but for late spruce 2 all compounds except α -pinene, eucalyptol and γ -terpinene remained fairly stable with increase in light (Appendix A, Fig. 3b).

3.4 Light-dependent fractions of different compounds

Whilst some compounds like isoprene and sabinene were specific for different tree species, the compounds α-pinene,
 camphene, 3-carene, limonene and eucalyptol were emitted from all of the measured leaves or needle twigs. As these compounds were emitted at different light levels, we will assess the light dependency of these compounds. The light-dependent fraction for isoprene was 100% for all of the isoprene emitting trees (Table 2). The same fraction and significance were also found for sabinene emission from beech (P<0.001, Table 2). The light response for the total MT emission differed between species. Whilst the oaks and the second early spruce showed little or no response to light, the beech and the

30 remaining spruce trees increased their emissions. The light-dependent fraction of other MTs however depended on the compound and the tree species. Camphene had a significant change in emission from darkness to 500 μ mol m⁻² s⁻¹ for early

and late spruce 2, but for remaining light levels camphene showed no clear light dependency for any of the measured trees (Appendix A, Table 1 and 2).

For the oaks, besides isoprene no other compounds showed a significant light dependency. For beech, some compounds like camphene, 3-carene, limonene and eucalyptol increased the light-dependent fractions with higher light levels, but without this being a significant increase in its emissions (Appendix A, Table 1 and 2).

The two provenances of spruce showed a higher light-dependent fraction for MTs in comparison to the broadleaved trees. Early spruce 1 and late spruce 1 showed light-dependent fractions of 76-86% and 67-94% respectively for the total MT emission (Table 2). Both trees had high light-dependent fractions for the compounds α -pinene, 3-carene and eucalyptol. For early spruce 1, eucalyptol increased its light-dependent fraction with increasing light levels. For late spruce 1 there was a

10 higher percentage of light dependency for α-pinene, but only limonene increased in light dependency with increasing light. Early spruce 2 had low light-dependent fractions for all compounds except eucalyptol, whilst late spruce 2 had high light-dependent fractions for α-pinene and eucalyptol. Although several of the above mentioned compounds from early spruce 2 and late spruce 2 showed a light dependency, this light dependency did not change with a change in light level (Table 2).

15 **3.5 Photosynthesis and stomatal conductance of oak, beech and spruce**

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For oak, the assimilation (A_n) rates were fairly similar between the two trees, ranging from -0.6 - -0.5 µmol CO₂ m⁻² s⁻¹ in darkness and 2.4-4.5 µmol CO₂ m⁻² s⁻¹ with light (Fig. 4a, Table 1). The difference was larger for the stomatal conductance (G_s): oak 1 showed a significant difference with increasing light (P<0.05) in comparison to oak 2 which showed higher internal variation (P>0.2). In regards to their photosynthetic and stomatal conductance ranges, they are comparable with studies performed on oak leaves grown in either shaded or semi-shaded conditions (Morecroft and Roberts, 1999; Valladares

- <u>et al., 2002).</u> For beech, A_n increased from darkness to the PAR level of 500 µmol m⁻² s⁻¹ (P<0.001), but did not show a response to further increase in light (P>0.6). A_n was between 3-3.6 µmol CO₂ m⁻² s⁻¹ with light and -0.3 µmol CO₂ m⁻² s⁻¹ in darkness, whilst G_s ranged between 100-400 mmol H₂O m⁻² s⁻¹ for all light levels (Fig. 4b).
- For early spruce 1, A_n was between 9.5-11.3 µmol CO₂ m⁻² s⁻¹ at a light level of 500 and 1000 µmol m⁻² s⁻¹ which decreased
 to 7.3 µmol CO₂ m⁻² s⁻¹ at 1500 µmol m⁻² s⁻¹. G_s followed a similar pattern, ranging from 1000-1200 mmol H₂O m⁻² s⁻¹ at a light level of 500 and 1000 µmol m⁻² s⁻¹ and decreased to 700 mmol H₂O m⁻² s⁻¹ at a light level of 1500 µmol m⁻² s⁻¹ (Fig. 4c, Table 1). A similar pattern as the BVOC emissions for early spruce 2 could also be seen in the rates of A_n and G_s with lower values coinciding with lower emissions, but which was significant only for A_n (Table 1). Late spruce 1 had a higher emission rate in comparison to late spruce 2, which was also evident for the A_n and G_s rates. Whilst late spruce 1 showed an increase
- 30 in both A_n and G_S with increasing light levels (P<0.05), late spruce 2 did not show any clear response to increasing light above 500 µmol m⁻² s⁻¹ (P>0.2). Late spruce 1 had an average A_n rate of 4.5-10.9 µmol CO₂ m⁻² s⁻¹ and an average G_S rate of 400-1100 mmol H₂O m⁻² s⁻¹ with light. For the second spruce, the A_n and G_S rates were stable at an average range of 3.6-5.1 µmol CO₂ m⁻² s⁻¹ and 300-500 mmol H₂O m⁻² s⁻¹ with light (Fig. 4d).

Overall, the investigated trees showed a similar response to light in their light dependent BVOC emissions, Λ_{μ} and G_{μ} , but the light level at which these processes saturate could vary for individual leaves or needle twigs.

4 Discussion

Light plays an important role as a driver of BVOC emissions, particularly in regards to *de novo* emissions. However, few studies have investigated in situ if the compounds emitted from different tree species respond similarly with a conditional change in light. Our aim was to investigate how different compounds responded to changing light conditions and if the response was similar between different tree species. Overall, the investigated trees showed a similar response to light in their light-dependent BVOC emissions, A_n and G_s , but the light level at which these processes saturate could vary for individual leaves or needle twigs.

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4.1 Responses of BVOC emissions to changing light conditions

Isoprene was the main emitted compound for the measured oak trees which showed a clear response to increasing light. This increasing emission with light has also been confirmed by other performed studies. Some compounds were species specific in regard to their emission rates, with high emissions of isoprene from English oak, sabinene from European beech and either α pinene or limonene by the provenances of Norway spruce. However, the compounds α pinene, camphene, 3 carene,

limonene and eucalyptol were emitted by all species, which made it possible to study how the light dependency of these compounds would differ between selected tree species.

All the trees with the capacity to emit isoprene showed a clear response to light, which has been confirmed by other studies as well (Tingey et al., 1981; Lehning et al., 1999; Grabmer et al., 2006). For beech, the main emitted compound was

20 <u>sabinene</u>, which also responded to increasing light. However, the light dependency of other compounds than isoprene differed depending on the tree species. The compound complete showed significant emission responses from early spruce 2 and late spruce 2, but only going from darkness to 500 μ mol m⁻² s⁻⁴. For the remaining trees, there was no clear camphene emission response to an increase in light. This suggests that this compound should be considered to be light independent when emission rates are to be modelled. Emission of camphene has been shown to be temperature dependent in a study on

25 Abies alba (Moukhtar et al., 2006).

A similarity which was found for the oaks and the beech was that apart from their main emitted compounds, the emission rate of other MTs did not show any significant response with increasing light (P>0.05). This observation would suggest that the emission of MTs from these deciduous trees should be regarded as light-independent instead of light-dependent, dividing the emissions into light-dependent and light-independent fractions. For coniferous tree species, which are known to have storage structures contributing to a considerable light-independent emission, a division Dividing the emitted compounds of the emissions into light-dependent and light-independent fractions has been suggested ev fractions has also been suggested

for Norway spruce, for which the light dependent emissions have been reported to range between 25.45% of the total emission rates (Ghirardo et al., 2010). Although similar structures are absent in the broadleaf species studied here, the results suggest that these species also have a light-independent fraction.

- The two provenances of spruce had different responses of their emitted compounds with an increase in light, where the light dependent fraction of the total MT emission increased for all trees except for early spruce 2. Regarding separate compounds, they were also shown to respond differently with an increase in light depending on the individual tree. The compound camphene showed significant emission responses from early spruce 2 and late spruce 2, but only going from darkness to 500 µmol m⁻² s⁻¹. For the remaining trees, there was no clear camphene emission response to an increase in light. This suggests that this compound should be considered to be light-independent when emission rates are to be modelled. Early spruce 1
- 10 showed light-dependent fractions from α-pinene, 3-carene, limonene and eucalyptol, but with eucalyptol being the only MT compound which continued to increase its light-dependent fraction with increasing light intensity. A similar light dependency of eucalyptol has also been found for emissions from *Abies alba* (Moukhtar et al., 2006). Early spruce 2 showed light-dependent fractions from α-pinene, camphene and eucalyptol. However, as the amount of samples taken on early spruce 2 were few, it is difficult to draw any clear conclusions for this tree. Both the late spruce trees had light-dependent
- 15 emissions of α -pinene and eucalyptol. Late spruce 1 also showed light-dependent fractions for 3-carene going from darkness to light, but the overall emission rate of this compound was low and of little importance in regard to the general compound contribution. For late spruce 2, α -pinene and camphene showed significant emission increases from darkness to 500 µmol m⁻² s⁻¹. The response of late spruce 2 might however be masked by high internal emission variation at 500 µmol m⁻² s⁻¹.

Regarding the light-dependency of MT emissions, there are several studies which have suggested that both de novo and

- 20 storage pool emissions can occur within different tree species (Dindorf et al., 2006; Moukhtar et al., 2006; Ghirardo et al., 2010). With the current experimental setup, it is only possible to make assumptions of the relative contributions of *de novo* sources and storage pools. This is otherwise often tested by using ¹³CO₂-labelling, where *de novo* emissions would have ¹³Cincorporated into their compound structures after a pulse of labelled ¹²CO₂-(Ghirardo et al., 2010). But by using genetically identical trees and fixed environmental conditions inside the measurement chamber, it has been possible to study the
- 25 emission response of different compounds to an increase in light intensity. Our study shows that different compounds respond differently to a change in light and that compounds like camphene have similar emission responses for English oak, European beech and Norway spruce and that all of the measured trees released isoprenoids in darkness, with emissions ranging from 0-0.4 µg gdw⁻¹ h⁻¹ for the broadleaf trees and 0.01-0.22 µg gdw⁻¹ h⁻¹ for the provenances of spruce. This would indicate that species such as English oak and European beech, which are considered to lack specific storage compartments,
- 30 have a capacity to store compounds in the mesophyll, which has also been suggested by other studies (Niinemets and Reichstein, 2003; Holopainen and Gershenzon, 2011). In a study by Loreto et al. (2000), ¹³C labelling was used on Holm oak (*Quercus ilex*) with and without illumination and found that the newly synthesized compounds could continue to be emitted long after initiation of darkness. It was suggested that the volatile compounds could be non-specifically stored within the plant leaves, either in the lipid phase or in the aqueous phase. Furthermore, Bäck et al. (2005) did a modelling study on Scots

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pine where a mesophyll pool was included, which enabled them to better capture diurnal and seasonal emission trends of MT emissions. These results suggest that as there might exist non-specific storage within the leaf tissue, *de novo* emitting tree species need to be considered to have storage pools in emission models as well. <u>However, wWith the current experimental setup</u>, it is only possible to make assumptions of the relative contributions of *de novo* sources and storage pools. This is

- 5 otherwise often tested by using ¹³CO₂ labelling, where *de novo* emissions would have ¹³C incorporated into their compound structures after a pulse of labelled ¹³CO₂ (Ghirardo et al., 2010). But by using genetically identical trees and fixed environmental conditions inside the measurement chamber, it has been possible to study the emission response of different compounds to an increase in light intensity.
- As many-models divide plants into categories or plant functional types depending on the growing conditions they have adapted to (Schurgers et al., 2011; Guenther et al., 2012), an approach looking at the emission patterns of separate compounds would perhaps improve the division of plant functional typesemission models further. If the plants are also categorized into the compound emission response, the model would perhaps provide more realistic values by dividing the compounds into light-dependent or independent fractions. The possibility of a converging behaviour in light dependences between different species is a promising idea, but further investigations are necessary to confirm this suggestion. We would
- 15 therefore strongly suggest that more studies assessing light dependency of different compounds are performed on similar or different tree species in order to verify this light dependency of the compounds.

4.2 Emission pattern variation and shade adaptation of the leaves and needle twigs

The European tree species presented here have distinct emission patterns: English oak is a known high isoprene emitter, European beech mainly emits MTs such as sabinene, and Norway spruce is known to emit both isoprene and MTs (Dindorf

- 20 et al., 2006; Ghirardo et al., 2010; Pokorska et al., 2012). The English oak clones in this study had emission rates between 3.5-18.3 μg gdw⁺h⁺ at a light level of 1000 μmol m⁻²s⁺ and a set temperature range of 18-21 °C. These emission rates are in line with the standardized emission rates reported by previous studies (Isidorov et al., 1985; Kesselmeier and Staudt, 1999; Pokorska et al., 2012; Persson et al., 2016). In regards to their photosynthetic and stomatal conductance ranges, they are comparable with studies performed on oak leaves grown in either shaded or semi shaded conditions (Morecreft and
- 25 Roberts, 1999; Valladares et al., 2002).-Between 96-99% of the total emission for oak consisted of isoprene, followed by MTs such as limonene and α-pinene. This compound contribution has not only been stable over three years of measurements on these genetically identical trees, but it is also in agreement with measurements at other sites (Staudt et al., 2001; Persson et al., 2016; van Meeningen et al., 2016). The low emission pattern variation This would suggest that even if environmental factors such as temperature or light influence the total emission from oak, these do not alter the compound contribution to a
- 30 great extent (Staudt et al., 2001; van Meeningen et al., 2016).

The European beech had an average total emission of 0.3 μ g gdw⁻¹ h⁻¹ in darkness and between 0.8 1.0 μ g gdw⁻¹ h⁻¹ with light. However, tThere were big differences in emission amounts between <u>beech</u> leaves, making it difficult to see any clear increase in BVOC emissions with an increase in light. When the light level exceeded 1000 μ mol m⁻² s⁻¹, there was also an

increase in SQT emissions. But as there was no obvious sign of injury and due to the low contribution of detected SQTs (<10%), we consider the leaves to be unstressed. The total emission rates are in the lower ranges in comparison to other studies with standardized emission rates (Moukhtar et al., 2005; Dindorf et al., 2006 and references therein). This could be because all samples were taken on the lowest positioned branches of the tree. In the study made by Persson et al. (2016) from the same site performed in 2013, the emission rates were taken at three different height levels within the canopy of all the above mentioned trees. For the European beech, the <u>standardized</u> emission rates were much higher at the top of the canopy in comparison to lower levels, with an average standardized emission rate found in this study could be caused by more shade-adapted leaves, with a possible lower capacity to respond to high increases in light. The levels of A_n and G_s presented here

- 10 are comparable with other studies performed on leaves adapted to shaded or semi-shaded conditions (Valladares et al., 2002; Warren et al., 2007; Scartazza et al., 2016). As the emission increase was unclear for the chosen light levels, more light levels between 0-500 µmol m⁻² s⁻¹ would be preferable. It would also be advisable to make more measurements at the top of the canopy in comparison to the lower levels in order to not underestimate the emission potentials for European beech. There were distinct differences in emission spectra between the two provenances of Norway spruce. The main emitted
- 15 compound for both provenances was isoprene, but regarding the emitted MTs early spruce was mainly a limonene emitter whilst late spruce emitted α -pinene. This emission pattern difference remained stable over three summer seasons for this sitebetween provenances has been observed in three separate studies performed at the same site (Persson et al., 2016 for 2013, unpublished data for 2014, current study for 2015). Furthermore, late spruce also emitted β -pinene at a higher rate than the early spruce trees, whilst the compounds α -terpinene and γ -terpinene were only emitted by late spruce. This would
- 20 suggest that for different provenances of the same species, different compound adaptations might exist. Studies on other tree species have suggested that trees can be divided into chemotypes depending on their emission patterns and that the compound contribution of these chemotypes remains fairly stable over time (Staudt et al., 2001; Bäck et al., 2012). This result is not surprising as trees would need to be able to adapt according to the local growing conditions.
- The average emission rates at 1000 μmol m⁻² s⁻¹ ranged between 0.1-0.6 μg gdw⁻¹ h⁻¹ for early spruce and 0.9-2.2 μg gdw⁻¹ h⁻¹
 ¹ for late spruce, which were in range of previous studies (Kesselmeier and Staudt, 1999; Grabmer et al., 2006). The four light levels that were tested did not provide enough information to address the light response entirely. More points taken between 0-500 μmol m⁻² s⁻¹ would therefore be advisable in order to fully understand the change in emission amounts. The second early spruce tree showed more fluctuation between different light levels, possibly as a response to stress exposure. When measurements were performed on this tree in 2013, the needles on the lowest branches dried and fell off after a
- 30 prolonged period without rain in the middle of July (Persson et al., 2016). In 2014, when measurements were performed again, the lower twigs had still not recovered and it was not possible to make any measurements on that level (unpublished data). In 2015, new twigs had started to emerge again on early spruce 2, but twigs were small and visibly less healthy. In comparison to the ten-year average weather conditions at the site, July in 2015 has had approximately the same amount of rainfall, but was almost 2 °C colder. It is likely that the weather conditions might have had an effect on the emission results.

However, as all trees have had the same exposure, it does not fully explain the different responses between trees. With less material to make measurements on and with possible recovery from stress, it is difficult to fully capture the release of BVOC emission from early spruce 2. The average A_n rates for early spruce and late spruce were between 4.3-12.1 and 3.6-12 µmol $CO_2 m^{-2} s^{-1}$ respectively, whilst the G_S rates ranged between 400-1200 mmol $H_2O m^{-2} s^{-1}$ for early spruce and between 300-1000 mmol $H_2O m^{-2} s^{-1}$ for late spruce. These values are in range or slightly higher than reported in other studies (Le Thiec et al., 1994; Roberntz and Stockfors, 1998; Špunda et al., 2005). Early spruce 1 and late spruce 2 behaved in a similar fashion as European beech with a tendency to stabilize their A_n and G_S rates at a light level of 500 µmol $m^{-2} s^{-1}$, indicating some shade adaptation of the selected needle twigs. Late spruce 1 increased both in A_n and G_S rates with light, possible because the tree stands more exposed than the others in the northeast corner of the IPG site and therefore is more light adapted in comparison to the other trees. Early spruce 2 showed the same fluctuating pattern in A_n and G_S rates as with the observed

BVOC emissions, most likely due to a restricted sample size and previous effect of drought stress on the tree.

5 Summary and conclusions

Measurements were performed on one European beech and on genetically identical mature individuals of English oak and two provenances of Norway spruce with the aim to study the light response of the emitted compounds. Our study shows that,

- 15 despite the existence of differences in emission amounts, the relative contribution of the main emitted compounds was similar between the individuals of the same tree species. Compounds like isoprene showed a light dependency for all of the measured isoprene-emitting trees, whilst camphene showed a slight response from early spruce 2 and late spruce 2 going from darkness to 500 µmol m⁻² s⁻¹ but no significant response for the remaining trees. Apart from isoprene for English oak and sabinene for European beech, there was no clear light dependency of other emitted isoprenoids which could show a
- 20 possible convergence in the response of these minor compounds to changes in light. For the provenances of spruce, some compounds like α-pinene, 3-carene and eucalyptol showed high light-dependent fractions for many of the individuals, which remained fairly stable with increasing light. This would possibly suggest that some MT compounds should be considered to be light-dependent in regard to emission models. As all measurements were performed on the lowest positioned branches of the tree, some trees showed indications of shade adaptation which could perhaps have inhibited the light response of certain
- 25 compounds. The low sample size could also be responsible for the difficulty in finding statistically significant increases of emissions with light. However, the study does show a potential convergence of the light responses for compounds such as camphene for all the studied trees and monoterpene emission from English oak and European beech. This convergence needs to be studied further both for the mentioned compounds and for other tree species in order to fill in potential knowledge gaps, but we believe that this could possibly be of significance to improve emission modelling.

Appendix

Appendix

5

Table A1. The mean average actual emission (\pm standard deviation) of detected compounds at light levels (PAR) 0, 500, 1000 and 1500 µmol m² s⁻¹ and the number of samples taken from English oak (*Quereus robur*), European beech (*Fagus sylvatica*) and the two provenances of spruce (*Picea abics*) in µg gdw⁻¹ h⁻¹. No data (n.d.) indicates that the compound was not detected in any sample for the measured light level on that particular tree.

			Trie	a. -			β.	3-	α-			Υ-			
		Isopre	yele	pinen	Camp	Sabin	pinen	Caren	terpin	Limo	Eucal	terpi	Linal		
Tree	PAR	ne	ne	e	hene	ene	e	e	ene	nene	yptol	nene	ool	SQT	Total
				$\frac{0.02 \pm}{0.02 \pm}$	0.03 ±			0.02 ±		0.08 ±	0.02 ±				0.16 ±
	0	n.d.	<0.01	<0.01	0.02	n.d.	n.d.	<0.01	n.d.	0.04	<0.01	n.d.	n.d.	n.d.	0.08
			<0.01												
		5.08 ±	÷	0.01 ±	0.01 ±			0.01 ±		0.05 ±	0.01 ±				5.19 ±
Oale 1	500	2.32	<0.01	0.01	0.01	n.d.	n.d.	<0.01	n.d.	0.03	0.01	n.d.	n.d.	n.d.	2.27
(n-15)			0.01												
(II=13)		12.53	±	0.01 ±	0.01 ±			0.01 ±		0.05 ±	0.01 ±				12.62
	$\frac{1000}{1000}$	± 3.68	<0.01	<0.01	0.01	n.d.	n.d.	0.01	n.d.	0.03	<0.01	n.d.	n.d.	n.d.	± 3.65
			0.01												
	1.500	16.31	±	$0.01 \pm$	$\frac{0.02 \pm}{0.02 \pm}$			$\frac{0.01 \pm}{0.01}$		$0.06 \pm$	$\frac{0.01 \pm}{100}$				16.43
	1500	± 2.91	<0.01	<0.01	0.01	n.d.	n.d.	<0.01	n.d.	0.03	<0.01	n.d.	n.d.	n.d.	± 2.86
-	-	-	-			-	-		-			-	-	-	-
	0			0.01 ±	0.01 ±			0.01 ±		0.03 ±	0.01 ±				0.05 ±
	θ.	0.02	<0.01	<0.01	<0.01	n.d.	n.d.	<0.01	n.d.	0.01	<0.01	n.d.	n.d.	n.d.	0.03
0.1.2	500	$\frac{2.68 \pm}{2.68 \pm}$	0.01	$0.01 \pm$	$\frac{0.04 \pm}{0.02}$			$\frac{0.01 \pm}{0.01}$		$\frac{0.08 \pm}{0.01}$	$\frac{0.02 \pm}{0.01}$				$\frac{2.79 \pm}{1.01}$
$\Theta a k z$	900	0.99	<0.01	0.01	0.02	n.d.	n.d.	0.01	n.d.	0.04	0.01	n.d.	n.d.	n.d.	1.01
(n=1/)	1000	$\frac{6.53 \pm}{2.0}$	0.01	$\frac{0.02 \pm}{0.01}$	$\frac{0.05 \pm}{0.02}$			$\frac{0.01 \pm}{0.01}$		$0.09 \pm$	$\frac{0.02 \pm}{0.01}$				$\frac{0.68 \pm}{1.05}$
	1000	2.0	0.01	0.02	0.02	n.d.	n.d.	<0.01	n.d.	0.02	<0.01	n.a.	n.d.	n.d.	5 70 -
	1500	3.08 ±	0.01	$\frac{0.03 \pm}{0.01}$	$0.04 \pm$			0.01 ±		$0.08 \pm$	$\frac{0.03 \pm}{0.01}$				$\frac{3.79 \pm}{2.14}$
	1500	2.22	0.01	<0.01	0.05	n.u.	n.u.	0.01	n.u.	0.00	<0.01	n.u.	n.u.	n.u.	0.25
	0	n d	n d	0.04 ±	$0.03 \pm$	n d	n d	0.04 ±	n d	$0.09 \pm$	$\frac{0.03 \pm}{0.01}$	n d	n d	n d	$\frac{0.23 \pm}{0.14}$
	Ð	n.u.	0.01	0.05	0.05	n.u.	n.u.	0.05	n.u.	0.00	0.01	11.u.	n.u.		0.14
			0.01	$0.04 \pm$	0.06 +	0.52 +		$0.02 \pm$		0.00 +	$0.04 \pm$				0.70 +
Booch	500	nd	$\overline{002}$	0.07 ±	0.00 ±	0.78	nd	0.05 ±	nd	0.07	0.04 ±	nd	nd	nd	0.76
(n-21)	200	n.u.	0.02	0.06 +	0.04 +	0.65 +	n.u.	0.03 +	n.u.	0.06 +	0.03 +	n.a.	n.u.	n.u.	1.23 +
(11-21)	1000	nd	0.01	0.00	0.02	0.07	nd	0.03	nd	0.00 -	0.05	nd	nd	0.02	1.18
ł	1000	n.u.	0.01	0.00	0.02	0.97	n.u.	0.05	n.u.	0.05	0.01	n.u.	n.u.	0.02	1.10
				$0.03 \pm$	0.03 +	$0.75 \pm$		0.03 +		0.07 +	0.03 +			+	0.00+
	1500	n.d.	0.01	0.03	0.03 ±	1.05	n.d.	0.05 -	n.d.	0.07 -	0.05 ±	n.d.	n.d.	0.06	1.05
								<0.01							
				0.01 ±	0.02 ±			±		0.01 ±	0.01 ±				0.05 ±
	θ	n.d.	n.d.	0.01	0.01	n.d.	n.d.	<0.01	n.d.	0.01	<0.01	n.d.	n.d.	n.d.	0.03
Forly														0.10	
- Early		0.18 ±		0.03 ±	0.02 ±		0.02 ±	0.06 ±		0.08 ±	0.04 ±			±	0.54 ±
spreee	500	0.03	n.d.	<0.01	0.01	n.d.	0.01	0.03	n.d.	0.01	0.01	n.d.	n.d.	0.07	0.04
(1 A														0.16	
(n=14)		0.21 ±		0.03 ±	0.02 ±		0.01 ±	0.04 ±		0.06 ±	0.05 ±			±	0.58 ±
	$\frac{1000}{1000}$	0.02	n.d.	0.01	0.02	n.d.	0.01	0.02	n.d.	0.01	0.01	n.d.	n.d.	0.08	0.09
		0.25 ±		$0.03 \pm$	$\frac{0.02 \pm}{0.02 \pm}$		$0.02 \pm$	0.01 ±		$0.05 \pm$	0.06 ±		0.14		$0.60 \pm$
	1500	0.03	<0.01	<0.01	0.01	n.d.	<0.01	<0.01	n.d.	<0.01	<0.01	n.d.	±	n.d.	0.05

													0.01		
-1	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_
			<0.01												
			±	0.02 ±	0.02 ±			0.01 ±		0.04 ±	0.01 ±				0.10 ±
	0	n.d.	<0.01	<0.01	<0.01	n.d.	n.d.	<0.01	n.d.	0.02	0.01	n.d.	n.d.	n.d.	0.04
Forly					<0.01										
Contraction		0.23 ±		$0.02 \pm$	±			0.01 ±		0.07_±	0.04 ±				0.37 ±
spruce	500	<0.01	n.d.	<0.01	<0.01	n.d.	n.d.	<0.01	n.d.	0.01	<0.01	n.d.	n.d.	n.d.	0.02
ź				0.01 ±	0.01 ±			0.01 ±			0.02 ±				0.12 ±
(n=13	+ 1000	0.05	n.d.	<0.01	0.01	n.d.	n.d.	<0.01	n.d.	0.01	0.02	n.d.	n.d.	n.d.	0.13
					<0.01										
		0.14 ±		0.03 ±	±		$0.02 \pm$	0.01 ±		0.04 ±	0.05 ±				0.29 ±
	1500	0.05	n.d.	<0.01	<0.01	n.d.	<0.01	<0.01	n.d.	<0.01	<0.01	n.d.	n.d.	n.d.	0.05
					0.03 ±					0.01 ±					0.04 ±
	0	n.d.	n.d.	<0.01	0.02	n.d.	n.d.	n.d.	n.d.	0.01	<0.01	n.d.	n.d.	n.d.	0.03
-		0.31 ±		$0.09 \pm$	$\frac{0.02 \pm}{0.02 \pm}$					$0.02 \pm$	$\frac{0.01 \pm}{0.01}$				0.49 ±
Late	500	0.13	<0.01	0.09	0.01	n.d.	0.01	0.01	0.01	0.03	0.01	n.d.	n.d.	n.d.	0.30
spruce)		0.01									0.10			
+	4000	1.26 ±	±	0.29 ±	0.21 ±		0.07 ±	$0.02 \pm$	$0.04 \pm$	$0.05 \pm$	$0.10 \pm$	±			2.16 ±
(n=13)	+1000	0.49	0.01	0.26	0.27	n.d.	0.03	0.01	0.02	0.05	0.05	0.06	n.d.	n.d.	0.84
			0.01									0.03			
	1500	$0.54 \pm$	±	$0.23 \pm$	$\frac{0.01 \pm}{0.01}$		$\frac{0.03 \pm}{0.03 \pm}$	$0.01 \pm$	$\frac{0.02 \pm}{0.02 \pm}$	$0.04 \pm$	$\frac{0.03 \pm}{0.03 \pm}$	±			0.93 ±
	1500	0.04	<0.01	0.01	<0.01	n.d.	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	n.d.	n.d.	0.04
-	-	-	-	-	-		-	-	-	-	-	-	-	-	-
	0			$\frac{0.02 \pm}{0.01}$	$\frac{0.03 \pm}{0.02}$			$\frac{0.04 \pm}{0.01}$		$0.04 \pm$	$\frac{0.01 \pm}{0.01}$				$0.25 \pm$
	Q	n.d.	n.d.	0.01	0.02	n.d.	n.d.	0.01	n.d.	0.02	0.01	n.d.	n.d.	n.d.	0.12
		0.20		0.14	<0.01		0.00	0.05		0.06	0.00				1.17
Late	500	$\frac{0.30 \pm}{0.16}$		$0.14 \pm$	±		$\frac{0.02 \pm}{0.02}$	$0.05 \pm$		0.06 ±	$\frac{0.02 \pm}{0.02}$				1.1/±
spruce	, 900	0.16	n.d.	0.07	<0.01	n.d.	0.02	0.04	n.d.	0.05	0.02	n.d.	n.d.	n.d.	0.70
²		0.45		0.00	<0.01		0.00	0.04		0.04	0.00	0.02			1.00
(n=18)	+ 1000	$\frac{0.45 \pm}{0.00}$		$\frac{0.20 \pm}{0.01}$	±		$\frac{0.03 \pm}{0.01}$	$\frac{0.06 \pm}{0.01}$		$\frac{0.06 \pm}{0.01}$	$\frac{0.03 \pm}{0.01}$	• *			$\frac{1.69 \pm}{0.12}$
<u> </u>	× 1000	0.00	n.a.	0.01	<0.01	n.a.	<0.01	<0.01	n.a.	0.01	<0.01	0.02	n.a.	n.a.	0.12
		0.22		0.015	<0.01		0.02	0.05		0.05	0.04	0.04			1.41
	1500	0.02	n d	0.013	-0.01	n d	0.03 ±	0.01	d	0.01	0.04 ± <0.01	-0.01	d	n d	1./11 ±
	1500	0.05	n.a.	± 0.04	<0.01	n.a.	0.01	0.01	n.a.	0.01	<0.01	<0.01	n.a.	n.a.	0.08

Table A1. The mean average actual emission (\pm standard deviation) of detected compounds at light levels (PAR) 0, 500, 1000 and 1500 µmol m⁻² s⁻¹ and the number of samples taken from English oak (*Quercus robur*) in µg gdw⁻¹ h⁻¹. No data (n.d.) indicates that the compound was not detected in any sample for the measured light level on that particular tree.

Tree		<u>Oak 1 (</u>	<u>n=15)</u>		<u>Oak 2 (n=17)</u>					
<u>PAR</u>	<u>0</u>	<u>500</u>	<u>1000</u>	<u>1500</u>	<u>0</u>	<u>500</u>	<u>1000</u>	<u>1500</u>		
<u>ISO</u>	<u>n.d.</u>	5.08 ± 2.32	12.53 ± 3.68	16.31 ± 2.91	0.02	2.68 ± 0.99	6.53 ± 2.0	<u>5.68 ± 2.22</u>		
Tricyclene	<u><0.01</u>	$\leq 0.01 \pm < 0.01$	$\underline{0.01 \pm {<} 0.01}$	$0.01 \pm < 0.01$	<u><0.01</u>	<u><0.01</u>	<u>0.01</u>	<u>0.01</u>		
<u>α-pinene</u>	$\underline{0.02 \pm <0.01}$	0.01 ± 0.01	$\underline{0.01 \pm {<}0.01}$	$0.01 \pm < 0.01$	$\underline{0.01 \pm <\!\! 0.01}$	$\underline{0.01\pm0.01}$	$\underline{0.02\pm0.01}$	$\underline{0.03 \pm <} 0.01$		
Camphene	$\underline{0.03\pm0.02}$	$\underline{0.01 \pm 0.01}$	$\underline{0.01\pm0.01}$	$\underline{0.02\pm0.01}$	$0.01 \pm < 0.01$	$\underline{0.04\pm0.02}$	$\underline{0.05\pm0.02}$	$\underline{0.04\pm0.03}$		
Sabinene	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
β-pinene	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
3-Carene	$0.02 \pm < 0.01$	$0.01 \pm < 0.01$	$\underline{0.01\pm0.01}$	$0.01 \pm < 0.01$	$0.01 \pm < 0.01$	$\underline{0.01\pm0.01}$	$0.01 \pm < 0.01$	$\underline{0.01 \pm 0.01}$		

<u>a-terpinene</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>
Limonene	$\underline{0.08\pm0.04}$	0.05 ± 0.03	$\underline{0.05\pm0.03}$	$\underline{0.06 \pm 0.03}$	$\underline{0.03 \pm 0.01}$	$\underline{0.08 \pm 0.04}$	$\underline{0.09 \pm 0.02}$	$\underline{0.08 \pm 0.01}$
Eucalyptol	$0.02 \pm < 0.01$	$\underline{0.01\pm0.01}$	$\underline{0.01\pm {<}0.01}$	$0.01 \pm < 0.01$	$0.01 \pm < 0.01$	$\underline{0.02\pm0.01}$	$0.02 \pm < 0.01$	$0.03 \pm < 0.01$
<u>y-terpinene</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>
Linalool	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>
<u>SQT</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>
Total	0.16 ± 0.08	<u>5.19 ± 2.27</u>	<u>12.62 ± 3.65</u>	16.43 ± 2.86	0.05 ± 0.03	<u>2.79 ± 1.01</u>	<u>6.68 ± 1.95</u>	<u>5.79 ± 2.14</u>

Table A2. The mean average actual emission (\pm standard deviation) of detected compounds at light levels (PAR) 0, 500, 1000 and 1500 µmol m⁻² s⁻¹ and the number of samples taken from European beech (*Fagus sylvatica*) in µg gdw⁻¹ h⁻¹. No data (n.d.) indicates that the compound was not detected in any sample for the measured light level on that particular tree.

Tree		Beech	(<u>n=21)</u>	
PAR	<u>0</u>	<u>500</u>	<u>1000</u>	<u>1500</u>
ISO	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>
Tricyclene	<u>n.d.</u>	<u>0.01 ± 0.02</u>	<u>0.01</u>	<u>0.01</u>
<u>a-pinene</u>	0.04 ± 0.03	0.04 ± 0.02	0.06 ± 0.06	0.03 ± 0.03
Camphene	0.05 ± 0.03	0.06 ± 0.03	0.04 ± 0.02	0.03 ± 0.02
Sabinene	<u>n.d.</u>	0.52 ± 0.78	<u>0.65 ± 0.97</u>	<u>0.75 ± 1.05</u>
<u>β-pinene</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>
<u>3-Carene</u>	0.04 ± 0.03	0.03 ± 0.02	<u>0.03 ± 0.03</u>	0.03 ± 0.02
<u>a-terpinene</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>
Limonene	0.09 ± 0.05	0.09 ± 0.07	0.06 ± 0.05	<u>0.07 ± 0.03</u>
<u>Eucalyptol</u>	0.03 ± 0.01	0.04 ± 0.01	<u>0.03 ± 0.01</u>	<u>0.03 ± 0.01</u>
<u>y-terpinene</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>
Linalool	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>
<u>SQT</u>	<u>n.d.</u>	<u>n.d.</u>	0.02	0.04 ± 0.06
<u>Total</u>	$\underline{0.25\pm0.14}$	0.79 ± 0.76	1.23 ± 1.18	<u>0.99 ± 1.05</u>

⁵

Table A3. The mean average actual emission (± standard deviation) of detected compounds at light levels (PAR) 0, 500, 1000 and 1500 µmol m⁻² s⁻¹ and the number of samples taken from the two provenances of spruce (*Picea abies*) in µg gdw⁻¹ h⁻¹. No data (n.d.) indicates that the compound was not detected in any sample for the measured light level on that particular tree.

Tree		Early spruc	e 1 (n=14)		Early spruce 2 (n=13)					
PAR	<u>0</u>	<u>500</u>	<u>1000</u>	<u>1500</u>	<u>0</u>	<u>500</u>	<u>1000</u>	<u>1500</u>		
ISO	<u>n.d.</u>	$\underline{0.18\pm0.03}$	$\underline{0.21 \pm 0.02}$	$\underline{0.25\pm0.03}$	<u>n.d.</u>	$0.23 \pm < 0.01$	<u>0.05</u>	$\underline{0.14 \pm 0.05}$		
Tricyclene	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u><0.01</u>	<0.01 ± <0.01	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
<u>a-pinene</u>	<u>0.01 ± 0.01</u>	$0.03 \pm < 0.01$	<u>0.03 ± 0.01</u>	$0.03 \pm < 0.01$	$0.02 \pm < 0.01$	$0.02 \pm < 0.01$	0.01 ± <0.01	$0.03 \pm < 0.01$		
Camphene	$\underline{0.02\pm0.01}$	$\underline{0.02\pm0.01}$	$\underline{0.02\pm0.02}$	$\underline{0.02\pm0.01}$	$0.02 \pm < 0.01$	$\leq\!\!0.01\pm\!<\!\!0.01$	$\underline{0.01\pm0.01}$	<u><0.01 ± <0.01</u>		

Sabinene	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
<u>β-pinene</u>	<u>n.d.</u>	0.02 ± 0.01	<u>0.01 ± 0.01</u>	$0.02 \pm < 0.01$	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	$0.02 \pm < 0.01$		
	<u><0.01 ±</u>									
3-Carene	<u><0.01</u>	$\underline{0.06\pm0.03}$	$\underline{0.04\pm0.02}$	$0.01 \pm < 0.01$	$0.01 \pm < 0.01$	$0.01 \pm < 0.01$	$0.01 \pm < 0.01$	$0.01 \pm < 0.01$		
<u>a-terpinene</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
Limonene	$\underline{0.01\pm0.01}$	$\underline{0.08\pm0.01}$	$\underline{0.06\pm0.01}$	$\underline{0.05 \pm {<}0.01}$	$\underline{0.04\pm0.02}$	$\underline{0.07\pm0.01}$	<u>0.01</u>	$\underline{0.04 \pm {<}0.01}$		
Eucalyptol	$0.01 \pm < 0.01$	$\underline{0.04\pm0.01}$	$\underline{0.05\pm0.01}$	$0.06 \pm < 0.01$	$\underline{0.01\pm0.01}$	$0.04 \pm < 0.01$	$\underline{0.02\pm0.02}$	$\underline{0.05 \pm {<}0.01}$		
<u>y-terpinene</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
Linalool	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	$\underline{0.14\pm0.01}$	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
<u>SQT</u>	<u>n.d.</u>	$\underline{0.10\pm0.07}$	$\underline{0.16\pm0.08}$	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
<u>Total</u>	$\underline{0.05\pm0.03}$	$\underline{0.54\pm0.04}$	$\underline{0.58\pm0.09}$	$\underline{0.60\pm0.05}$	$\underline{0.10\pm0.04}$	<u>0.37 ± 0.02</u>	$\underline{0.12\pm0.13}$	$\underline{0.29\pm0.05}$		
Tree		Late spruc	e 1 (n=13)		Late spruce 2 (n=18)					
PAR	<u>0</u>	<u>500</u>	<u>1000</u>	<u>1500</u>	<u>0</u>	<u>500</u>	<u>1000</u>	<u>1500</u>		
ISO	<u>n.d.</u>	$\underline{0.31 \pm 0.13}$	$\underline{1.26\pm0.49}$	$\underline{0.54 \pm 0.04}$	<u>n.d.</u>	$\underline{0.30\pm0.16}$	$\underline{0.45\pm0.06}$	$\underline{0.33 \pm 0.03}$		
Tricyclene	<u>n.d.</u>	<u><0.01</u>	$\underline{0.01\pm0.01}$	$0.01 \pm < 0.01$	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
<u>a-pinene</u>	<u><0.01</u>	$\underline{0.09\pm0.09}$	$\underline{0.29 \pm 0.26}$	$\underline{0.23\pm0.01}$	$\underline{0.02\pm0.01}$	$\underline{0.14 \pm 0.07}$	$\underline{0.20\pm0.01}$	$\underline{0.02 \pm 0.04}$		
Camphene	$\underline{0.03\pm0.02}$	$\underline{0.02\pm0.01}$	$\underline{0.21 \pm 0.27}$	$0.01 \pm < 0.01$	$\underline{0.03\pm0.02}$	<0.01 ± <0.01	$\leq\!\!0.01\pm\!<\!\!0.01$	$\leq 0.01 \pm < 0.01$		
Sabinene	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
<u>β-pinene</u>	<u>n.d.</u>	<u>0.01</u>	$\underline{0.07\pm0.03}$	$0.03 \pm < 0.01$	<u>n.d.</u>	0.02 ± 0.02	$0.03 \pm < 0.01$	$\underline{0.03 \pm 0.01}$		
<u>3-Carene</u>	<u>n.d.</u>	<u>0.01</u>	$\underline{0.02\pm0.01}$	$0.01 \pm < 0.01$	$\underline{0.04\pm0.01}$	$\underline{0.05\pm0.04}$	$0.06 \pm < 0.01$	$\underline{0.05\pm0.01}$		
<u>a-terpinene</u>	<u>n.d.</u>	<u>0.01</u>	$\underline{0.04\pm0.02}$	$0.02 \pm < 0.01$	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
Limonene	$\underline{0.01\pm0.01}$	$\underline{0.02\pm0.03}$	$\underline{0.05\pm0.05}$	$0.04 \pm < 0.01$	$\underline{0.04\pm0.02}$	$\underline{0.06\pm0.05}$	$\underline{0.06\pm0.01}$	$\underline{0.05\pm0.01}$		
Eucalyptol	<u><0.01</u>	$\underline{0.01\pm0.01}$	$\underline{0.10\pm0.05}$	$\underline{0.03\pm {<}0.01}$	$\underline{0.01\pm0.01}$	$\underline{0.02\pm0.02}$	$0.03 \pm < 0.01$	$\underline{0.04 \pm {<}0.01}$		
<u>y-terpinene</u>	<u>n.d.</u>	<u>n.d.</u>	$\underline{0.10\pm0.06}$	$0.03 \pm < 0.01$	<u>n.d.</u>	<u>n.d.</u>	$\underline{0.02\pm0.02}$	$\underline{0.02\pm0.02}$		
Linalool	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
<u>SQT</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>		
Total	0.04 ± 0.03	0.49 ± 0.30	2.16 ± 0.84	0.93 ± 0.04	0.25 ± 0.12	1.17 ± 0.70	1.69 ± 0.12	1.41 ± 0.08		

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Table 1: The P-values from repeated measures ANOVA tests on the emission rate of each compound, photosynthetic rates (A_n) and stomatal conductance (G_S) in response to an increase in light intensity. The trees that were measured were two individuals of English oak (*Quercus robur*), one European beech (*Fagus sylvatica*), two individuals of Norway spruce (*Picea abies*) with an early budburst (Early spruce) and two individuals of Norway spruce with a late budburst (Late spruce). P-values marked in bold show statistically significant values (P<0.05). Isoprene was not detected from the European beech tree.

Compound	Oak 1	Oak 2	Beech	Early spruce 1	Early spruce 2	Late spruce 1	Late spruce 2
Isoprene	<0.001	<0.001	-	<0.001	0.13	<0.001	<0.001
α-pinene	0.15	0.99	0.98	0.02	0.03	0.18	<0.001
Camphene	0.57	0.88	0.35	0.56	0.01	0.55	0.01
3-carene	0.43	0.90	0.92	0.01	0.29	0.05	0.36
Limonene	0.66	0.97	0.65	<0.001	0.46	0.59	0.40
Eucalyptol	0.39	0.86	0.61	0.004	0.01	<0.001	0.07
Total BVOCs	<0.001	<0.003	0.87	<0.001	0.23	0.01	0.003
An	<0.001	<0.001	0.001	<0.001	0.03	0.001	<0.001
Gs	0.02	0.23	0.25	0.007	0.13	0.02	<0.001

Table 2: The percentage of emissions that are dependent on light (PAR, in μ mol m⁻² s⁻¹), as determined for the total monoterpene (MT) emission and for the main emitted compounds. The percentage was calculated as 100% × (light emissions - dark emissions)/light emissions. The numbers in brackets are the standard error of the mean. The trees that were measured were two individuals of English oak (*Quercus robur*), one European beech (*Fagus sylvatica*), two individuals of Norway spruce (*Picea abies*) with an early budburst (Early spruce) and two individuals of Norway spruce with a late budburst (Late spruce). No data (n.d.) indicates compounds that were not detected in any sample or light level for that particular tree.

Tree	PAR	Total MT	Isoprene	α-pinene	Camphene	Sabinene	3-Carene	Limonene	Eucalyptol
	500	0 (0)	100 (0)	0 (0)	17 (10)	n.d.	0 (0)	0 (0)	0 (0)
Oak 1	1000	4 (4)	100 (0)	0 (0)	17 (17)	n.d.	11 (11)	5 (5)	0 (0)
	1500	10 (10)	100 (0)	0 (0)	40 (21)	n.d.	0 (0)	9 (9)	3 (3)
	500	0 (0)	100 (0)	0 (0)	15 (10)	,	21 (21)	0 (0)	0 (0)
Oak 2	500	0(0)	100 (0)	0(0)	15 (10)	n.d.	21 (21)	0(0)	0(0)
oun 2	1000	15 (15)	100 (0)	16 (16)	20 (20)	n.d.	31 (18)	15 (15)	13 (13)
	1500	0 (0)	100 (0)	12 (6)	8 (8)	n.d.	0 (0)	0 (0)	0 (0)
	500	6 (6)	n.d.	0 (0)	0 (0)	100 (0)	0 (0)	0 (0)	0 (0)
Beech	1000	23 (10)	n.d.	20 (20)	4 (4)	100 (0)	15 (15)	0 (0)	0 (0)
	1500	52 (26)	n.d.	7 (7)	31 (31)	100 (0)	50 (6)	77 (23)	19 (19)
E	500	81 (5)	100 (0)	64 (9)	6 (6)	n.d.	88 (10)	84 (1)	89 (6)
spruce 1	1000	76 (6)	100 (0)	54 (8)	10 (10)	n.d.	79 (18)	79 (1)	89 (5)
~ F	1500	86 (3)	100 (0)	60 (8)	14 (9)	n.d.	73 (14)	76 (3)	91 (4)
	500	18 (4)	100 (0)	20 (8)	0 (0)	n d	15 (15)	18 (3)	69 (3)
Early	1000	0.00	100 (0)	2 (2)	8 (8)	n.d.	26 (26)	0 (0)	67 (4)
spruce 2	1000	0(0)	100 (0)	5 (5)	8 (8)	n.a.	20 (20)	0(0)	62 (4)
	1500	19 (14)	100 (0)	43 (10)	0 (0)	n.d.	7(7)	0 (0)	74 (3)
Late	500	67 (14)	100 (0)	98 (2)	12 (12)	n.d.	100 (0)	31 (25)	95 (5)
spruce 1	1000	94 (3)	100 (0)	67 (33)	45 (33)	n.d.	100 (0)	65 (32)	100 (0)
	1500	87 (3)	100 (0)	98 (2)	0 (0)	n.d.	100 (0)	79 (16)	100 (0)
Late	500	26 (15)	100 (0)	85 (1)	0 (0)	n.d.	16 (13)	8 (8)	57 (22)
spruce 2	1000	68 (8)	100 (0)	91 (3)	0 (0)	n.d.	40 (8)	37 (18)	78 (14)
	1500	57 (13)	100 (0)	85 (5)	0 (0)	n.d.	23 (12)	20 (20)	77 (15)

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Fig. 1: The total BVOC emission rate of two individual English oak trees (open circles) and the relative contribution of the major compounds at four intensities of photosynthetically active radiation (PAR). The error bars show the standard deviation, n = 3-5 leaves. The category "Other" contains the compounds tricyclene, camphene and eucalyptol.

Fig. 2: The total BVOC emission rate for European beech (open circles) and the relative contribution of the major compounds at four intensities of photosynthetically active radiation (PAR). The error bars show the standard deviation, n= 4-6 leaves. The category "Other" contains the compounds tricyclene, and eucalyptol.

Fig. 3: The total BVOC emission rate from two individuals of Norway spruce with an a) early budburst and with b) a late budburst and the relative contribution of the major compounds at four intensities of photosynthetically active radiation (PAR). The open circles show total monoterpene emission, whilst the open squares show isoprene emission of all measured twigs (n = 3-6 twigs). The error bars are the standard deviation of the data. The category "Other" contains the compounds tricyclene, β -pinene, eucalyptol and linalool for early spruce and tricyclene, β -pinene, α -terpinene eucalyptol and γ -terpinene for late spruce.

Fig. 4: The net assimilation rate (An) and stomatal conductance (G_S, mmol H₂O m⁻² s⁻¹) of a) two individuals of English oak, b) European beech, c) two individuals of Norway spruce with an early budburst (Early spruce) and d) two individuals of Norway spruce with a late budburst (Late spruce). The values are averages ± the standard deviation (n = 13-21).