Author's response on the comments by Anonymous Referee # 1 on

"Tree water relations trigger monoterpene emissions from Scots pine stem during spring recovery" by A. Vanhatalo et al.

We thank Referee #1 for relevant comments and response to them below.

P7787 lines 1 and 26, does "temperature" refer to ambient temperatures?

Response: On line 1 (and figure 1), temperature refers to ambient air temperature. On line 26, the temperature normalization was conducted using air temperature measured inside the stem enclosure. We will edit the sentences: "The ambient temperature, snow depth…" and "The stem CO_2 efflux was temperature-normalised using the temperatures measured inside the enclosure to study…"

P7787 lines 10 -14, What is the approximate age of the tree and the shoots being measured?

Response: The tree is about 50 years old and the shoot chamber enclosed shoot growth of two to three years, in length 10–15 cm.

Figure 4 line width is difficult to see relative to the other figures.

Response: We will edit the figure 4 to make it more readable.

Author's response on the comments by Anonymous Referee # 2 on
"Tree water relations trigger monoterpene emissions from Scots pine stem during spring recovery" by A. Vanhatalo et al.

We thank Referee # 2 for devoting the time to review our paper. We have done our best to response the comments (see below).

The manuscript of Vanhatalo et al. reports of a monoterpene emission burst induced in April in a Scotch pine tree following recovery from winter freezing. Although this manuscripts raised a potentially interesting ecological issue on VOC emission, it is based on measurements run in ONLY ONE TREE! Therefore, this manuscript provides just indications of an evidence occurred for two year consecutively in only one tree because more biological replicates are required to claim for a physiological mechanism. Indeed biological replicates of many (i.e. 3-5) trees are needed otherwise how the authors can be sure that such an event (springtime burst of monoterpenes) identify a mechanism occurring in all the trees or it is just an anomaly happening for some reasons in just this particular investigated tree? On the other hand, if the burst of monoterpenes measured by the authors regards (and occur in) all the Scots pine tree of a forest, a validation should be found also at canopy level with eddy covariance flux measurements. In addition, the authors refer many times throughout the text to either summertime or daily/hourly time-resolved measurements, although no summertime and daily/hourly time-resolved data have been shown. Besides, the authors discussed about the 'tree water relations' without showing evapotranspiration flux data that have been measured by the same device that measure the CO2 exchange (as stated by the authors in line 18 page 4). Therefore, in order to make the manuscript acceptable for publication, I suggest the authors to add some more biological replicates and/or a validation of the monoterpenes burst through eddy covariance flux measurements, and to address my major (and minor) revisions listed below.

Response: Thank you for this comment. We are well aware that our arguments would be better justified if we had data on more trees. While our measurement site is well instrumented and usually has replicate measurements, in this case we can unfortunately only present data from one tree. Since we use here many measured tree-scale parameters, the combination of all necessary measurements was available on only one tree at the time. However, despite of the lack of biological replicates, the measurements from two consecutive years show fairly similar features, and therefore we are confident that our observations are related to the intrinsic seasonal physiology of the pine trees and that they are significant in the springtime BVOC dynamics of the trees. We have tried to clarify this in the text.

Earlier at the same site, high monoterpene emissions from pine shoots have been observed in springtime (Hakola et al. 2006, Aalto et al. 2014). Comparison to the ecosystem scale flux measurements was done, but no clear correlation between ecosystem scale fluxes and chamber measured fluxes could be seen. Since the ecosystem scale measurements upscale the emissions of the whole stand, such transient physiological features related to emission changes in individual trees are easily lost in the measurement noise. As the environmental factors vary within the stand (most importantly melting of snow cover and sunfleck-related rapid temperature changes), and the tree individuals exhibit naturally somewhat different responses to these factors, this produces variance in timing of the physiological processes within the stand. Furthermore, the footprint of the ecosystem-scale flux measurements is large and within the footprint there are several tree species (Norway spruce, Common juniper and several broadleaved species) and also moister and drier site types. Moreover, since many monoterpenes are very rapidly reacting in the atmosphere especially

under spring conditions they may not be detectable above the canopy with eddy covariance or other micrometeorological measuring systems.

The referee is correct that transpiration data is not shown in figures though it is discussed shortly in the text. To attain good quality transpiration data the relative humidity of air must be rather low. In natural boreal conditions in spring this is not too often the case, and thus good quality data lacks in many cases, especially in night-time. This is why we show sap flow and VPD instead, which both reflect nicely how much a tree loses water to the atmosphere, also when relative humidity is high. The transpiration mention was removed from the abstract and it is mentioned once in the results section with a note that data is not showed in any figure.

MAJOR REVISIONS

All the sub-paragraphs of the 'discussion' section look too much as an introduction or as a chapter for a textbook. I suggest the author to shorten the text and focus all these sub-paragraph more on the explanations that can be supported by the data shown in this manuscript.

Response: Thanks, you have a good point here. However, as the paper is discussing a totally novel finding, we wanted to explore the most important physiological processes possibly affecting it. That is why we present some parallel explanations. We have now revised the Discussion to overcome such an interpretation, and condensed the text in order to concentrate on the most plausible issues.

Conclusion section must be dramatically reduced to a few sentences without citations.

Response: Revised according to suggestion.

Lines 24-25, page 9 and lines 26-27, page 14: no statistical treatment have been performed to evaluate to strength of the relationships between the dynamics of the different variables (i.e. ANOVA).

Response: Due to lack of replicates (as the referee correctly noticed) and the nature of the dataset showing phenomena occurring only in a specific time, it is impossible to do statistics to verify the results. However, as the phenomenon was repeated in two consecutive springs with similar timing and very similar environmental responses, we suggest that at least a close relationship between the monoterpene burst and the presented variables exists.

I suggest the authors to cut the Y-axis to enlarge the lower part of figure 3B; moreover, I suggest the authors to merge panel E, F of Fig. 3 to panel A, B of Fig. 1.

Response: Fig 3B was revised. However, Fig 3 shows conditions inside the enclosure affecting emissions during the measurements, while Fig 1 shows the ambient conditions affecting the tree spring recovery at stand scale. Therefore we feel that the right place to enclosure temperature is in Fig 3, and have not merged the figures.

I suggest the author to remove Figure 6 as it is redundant, because the same information are shown already in Fig. 4C, D.

Response: It is true that the same data is partly presented in two figures, but figure 4 shows short-term dynamics, whereas the figure 6 points out the seasonal change until summer and the onset of sap flow around the time of monoterpene burst.

MINOR REVISIONS

Lines 12-15, page 1: the author should consider also VOC emission from the soil.
Response: During the time of observed monoterpene burst, the soil was covered with snow and there were no ongoing VOC measurements yet: the soil enclosures to study VOCs are installed only after snow melt. From earlier studies (e.g. Aaltonen et al. 2011, 2012) we know that snowpack hinders the emissions and once snow has melt, the soil emits VOCs at a rather high rate. However, we added the soil and understory vegetation as potential large sources for VOCs in the abstract.

Line 15, page 1: the authors mentioned 'anomaly', but refer to what? How is defined the 'normality'?
Response: Changed 'anomaly' to 'high emission rates'.

Line 20, page 1: no 'transpiration' data have been shown (see my comments above).
Response: This issue is discussed above.

Line 21, page 1: again, the authors mentioned 'unusual', 'anomalous', but refer to what? How is defined the 'normality'?
Response: We have revised this to 'non-systematic'.

Line 27, page 1: '20-50%' in weight?
Response: Yes, per weight basis. This was added.

Line 28, page 1: '0.5%' in weight?
Response: Yes, per weight basis. Text was revised.

Lines 17-18, page 2: please add Loreto et al. PNAS (1996).
Response: Added.

Lines 9-10, page 3: This is absolutely not enough! Because (in addition to what said above), the tree can be visibly healthy, but can have anomalies inside…
Response: We added wording indicating potential biotic or abiotic damages as sources for high transient emissions. However, here we mainly refer to emissions that are not triggered by any external factors.

Line 22, page 4: please indicate which kind of gas standard.
Response: The following text was added: 'The replacement of the gas analysers did not cause any irregularity in the H_2O and CO_2 exchange data because the calculation of gas exchange is primarily dependent on concentration difference instead of absolute concentration. Both analysers were also calibrated for CO_2 using a comparable calibration method and standard gases containing ca. ambient concentration of CO_2. For more details on CO_2 and H_2O calibration protocol used at SMEAR II, see Keronen et al. (2014).'

Lines 24-26, page 4: either add a reference or report the formula of the exponential curve mentioned.
Response: The formulas for the exponential curves were added.

Lines 30-31, page 4: replace "molecular masses were measured" with "protonated mass ions were monitored".
Response: Replacement done.

Lines 2-4, page 5: please add more details of PTR-MS calibration; has a gas standard been used?
Response: Revised, and the following text added: 'A mixture of several VOCs (e.g. α-pinene as a representative of monoterpenes) in nitrogen was used as a gas standard. The mixture was further diluted with volatile-free air from a zero air generator to attain concentrations below 20 parts per billion by volume, i.e. around the ambient atmospheric concentrations.'

Line 4, page 5: why 'other'?
Response: Word 'other' removed from the text.

Line 7, page 5: please show the 'temperature normalization equation'.
Response: The equation was added to the text.

Line 12, page 5: 'for this purpose', but which one do the author mean?
Response: We mean that the chamber was tailored to study reactive gas fluxes from tree stems. The text is now specifying this.

Line 12, page 7: where these 'maximum' and 'minimum' data have been shown?
Response: The daily pattern of emission rates are shown in Figure 3A,B and Fig 4A, B. Reference to the figure 4 was added which led to change the order of the figures: previous figure 4 is now 5 and vice versa.

Lines 24-30, page 7: daily data have not been shown (see my Major revision above).
Response: The daily emission data is shown in Figure 4, and a reference to this figure has been added.

Lines 4-5, page 8: Why this should be a result?
Response: This was moved to the materials and methods section.

Lines 13, page 8: how the authors can claim for 'an acclimation response'?
Response: The text was revised and 'acclimation response' was left out.

Line 21, page 8: again, no data having such a time-resolution have been shown.
Response: The time lag approximation was removed from here.

Lines 24, page 8: 'consistantly'?
Response: Word removed as unnecessary.

Lines 13-15, 26-29 page 9 and line 1, 3 page 10: the authors keep referring to hourly, daily, summertime data not shown in this manuscript.
Response: The hourly resolved data is shown in Fig 5 a, b. Summer-time data on radial change fluctuations is not presented in this manuscript as the focus is in spring-time phenomenon.

Lines 9-12, page 10: besides this sentence is puzzling, which are the 'driving forces'?
Response: We have modified the sentence. 'Driving force' is transpiration.

Lines 12-15, page 10: how can the authors be so sure that ‘winter embolism’ occurred in this particular study case?

Response: We cannot be sure, but winter embolism formation is known to be a common occurrence in trees, including Scots pine, (e.g. Sperry, John S., and David J. Robson. "Xylem cavitation and freezing in conifers." *Conifer cold hardiness*. Springer Netherlands, 2001. 121–136). The text was edited and the reference added.

Lines 27-28, page 10: why ‘stem CO2 flux anomalies might be related to this phloem activity’?

Response: Because phloem takes part in embolism refilling. Refilling requires metabolic activity which should increase stem respiration and CO_2 efflux rate.

Lines 10-11, page 11: delete this sentence.

Response: Done.

Figure 4: why ‘VPD data of 2013’ are missing in Figure 4?

Response: Figure is supplemented with more VPD data.

Author's response on the comments by Anonymous Referee # 3 on
"Tree water relations trigger monoterpene emissions from Scots pine stem during spring recovery" by A. Vanhatalo et al.

We thank Referee # 3 for relevant and constructive comments. Below, we respond to them one-by-one.

The manuscript represents another interesting and useful contribution from one of the Finnish field sites, here the Scots pine ecosystem. It is a representative, heavily instrumented environment, and the new work is an innovative study relating plant seasonal dynamics to potential atmospheric impacts. The experiment is well described, and a series of relevant auxiliary measurements were conducted to aid in interpretations. The weaknesses of the study lie in the lack of reproduction (only one tree studied), and the associated speculation concerning the results and their drivers. Since this is likely ongoing work, I recommend including another season (spring 2014, 1015 ?) and possibly more trees into the manuscript when ready, and/or reduce the amount of speculation by focusing on the most likely reasons for the observations, clearly indicating what is known and what is speculation. The title should be changed accordingly.

Response: Thank you for this suggestion. We agree that our data is limited by the lack of biological replicates, but in our opinion it still offers a novel insight and important information on a previously unknown relation between VOCs and tree water transport. We have two years of data from the same tree, which gives us confidence that the phenomenon is not a measuring artefact or an anomaly of one time. Given that other published studies on this issue don't exist, we believe that this study could already with the present datasets serve as a key for other researchers to plan measurements confirming our results. In the future, we'll be able to confirm whether this phenomenon is a general feature of Scots pines.
The title was not changed.

Specific comments:
1. I agree that terpene emissions from tree stems of terpene-storing species is a worthwhile study subject. However, it should be more prominently compared to the other, presumably more relevant sources of terpenes to the atmosphere. The authors compare only to the dominant source of emissions, namely foliage. They should include the other identified sources that add/modulate the total terpene source: (i) leaf litter on the soil, (ii) herbivore impacts, and (iii) forest management, aka selective thinning/removing and harvesting. All these have been studied and published works exist. If the current study's findings indicate that stems are minor but significant sources, either via the demonstrated short-term effect or via all-year-round emissions, then this should be related to the other minor sources. The comparisons are, in my opinion, much more relevant here than the yet still speculative nature of the origin and drivers of stem emissions; future work could instead focus on the more relevant sources.

Response: We understand the question very well, and agree that the full analysis of VOC exchange between a forested ecosystem and atmosphere should include all potential sources, for example soil and leaf litter, and the biotic and abiotic disturbances, in addition to the traditional tree canopy approach. At our field site we have performed long-term measurements of different ecosystem components influencing the terpene budget at stand scale. We are also pioneering in the stem VOC exchange measurements under field conditions. This paper was narrowed to deal only with the springtime events in stem VOC exchange, in order to focus on the *in situ,* transient

physiological processes linking the monoterpene emissions and tree water transport. This was a conscious decision as otherwise the paper would have been expanded to several new aspects of field and the paper already utilizes lots of datasets. The seasonal cycle of stem-originating VOC emissions and their role in ecosystem-scale VOC budget will be discussed in other papers which we are currently working with.

2. Related to #1, above-canopy flux measurements, which have been done at this site in the past, should be included if available to put the observations into context.

Response: Comparison to the ecosystem scale flux measurements was done, but no clear correlation between ecosystem scale fluxes and chamber measured fluxes could be seen. This is most probably because of many reasons: the trees are individuals with different genomes and thus they show different reactions to environmental factors, which produces variance in timing and strength of the physiological processes. Moreover, though trees grow in the same forest stand, they experience slightly different environment: some get more light than others, at some points snow cover is thinner and melts faster etc. Summing up, the timing of the rather transient (about 12 h) monoterpene burst might vary within the forest and thus its effect cannot necessarily be seen in ecosystem-scale measurements. Furthermore, the footprint of the ecosystem-scale flux measurements is large and within the footprint there are several tree species and site types. Moreover, monoterpenes react in the atmosphere and may not be detectable any more above the canopy with eddy covariance or other micrometeorological measuring systems.

3. The results are well summarized but could be combined with the discussion, realizing that some of the discussion is speculative. Comparative evaluations should be considered when discussing the fluxes. The same units of flux should be maintained, and switching like on page 7791, first paragraph, is discouraged.

Response: We have revised the Discussion and believe that most of the speculative issues are now either removed or clarified. For comparison purposes, also the shoot flux data is presented. By showing fluxes per day we wanted to point out how the peaks affect cumulatively to the fluxes. Nevertheless, the paper aims to weight the relation between the fluxes and the water transport, not the absolute levels of fluxes or water transport.

4. The discussion part is where most issues are. I think most of the discussion in section 4 until page 7795 is reasonable. It stems from the observations and is related to what is known about tree physiology during that time of the season. However, I strongly encourage the authors to consider eliminating, or at least drastically shortening sections 4.1 to 4.3. Temperature is obviously not relevant in the burst other than triggering seasonal sap-flow recurrence / end of dormancy, section 4.2 appears entirely speculative, and section 4.3 is so at least in parts. I am not even sure that the offered explanations are exclusive of additional possibilities, such as, I speculate, the reallocation of monoterpenes through sap-flow from roots to other tissue in spring (which could have been tested by an additional enclosure lower on the tree stem). It appears to me that much more research is needed to evaluate the most likely source and drivers of the monoterpene burst, and I think the authors should be satisfied with having discovered it, and linked it to the physiological

changes the tree underwent as it recovered from winter dormancy. I thus recommend shortening section 4 appropriately.

Response: Since the manuscript is concentrating mainly on the unexpected high monoterpene emission peaks, we'd like to include a discussion of three potential mechanisms triggering them (Ch 4.1–4.3). In our opinion, this analysis is valuable in interpreting the role of different physical and physiological phenomena in the monoterpene emissions from the stems. With this analysis, we can rather confidently rule out a direct effect of temperature, which is the main driver for emissions from foliage during most of the year. Due to lack of detailed monoterpene concentration measurements inside the tracheids, it is impossible to reach a final conclusion, but at the moment the refilling of embolized tracheids seems to be the most likely cause for these high peaks.
We have revised and shortened the Discussion to remove speculation and to clarify the most important findings. Reallocation from roots was included as one potential (albeit unlikely) source.

5. The conclusions need to address the relevance of the discovery, such as for spring atmospheric BVOC emissions and/or spring herbivore vulnerability or attacks. If the study can be reproduced, a focus on this relevance maybe useful in improving study design and auxiliary measurements.

Response: Conclusions are revised to include this aspect as well.

Tree water relations can trigger monoterpene emissions from Scots pine stem during spring recovery

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Abstract

Tree canopies are known to emit large amounts of VOCs (volatile organic compounds) such as monoterpenes to the surrounding air. High VOC emission rates from boreal forest~~tree canopie~~s have been observed during transition from winter to summer activity. The most important~~ain~~ source~~s~~ for these ~~is~~ are considered to be the green ~~biomass, i.e.~~ foliage, understor~~e~~y vegetation and soil organisms, but emissions from the living stand woody compartments have so far not been quantified. ~~A VOC emission anomaly has been observed during transition from winter to summer activity.~~ We analyzed if the non-foliar components could partially explain ~~the anomaly~~the springtime high emission rates. We measured the ~~VOC~~ monoterpene emissions from Scots pine (*Pinus sylvestris* L.) stem~~s~~ and shoots during the dehardening phase of trees in field conditions in two consecutive springs. We observed a large, transient monoterpene burst from the stem~~s~~, while the shoot monoterpene emissions ~~and transpiration~~ remained low. The burst lasted about 12 hours. Simultaneously, an unusual night-time sap flow and a~~n~~ ~~anomalous~~ non-systematic diurnal pattern of tree diameter were detected. Hence, we suggest that the monoterpene burst was a consequence of the recovery of the stem from winter-time, and likely related to the refilling of embolized tracheids and/or phenological changes in the living cells of the stem. This indicates that the dominant processes and environmental drivers triggering the monoterpene emissions are different between the stem~~s~~ and the foliage.

1 Introduction

The stems of mature coniferous trees contain significant quantities of oleoresin. 20–50% per weight of the conifer oleoresin consists of monoterpenes (Langenheim, 2003), and the monoterpene content of ~~dry~~ Scots pine (*Pinus sylvestris* L.) wood is about 0.5% (from dry weight) (Strömvall and Petersson, 2000). In addition to the volatile monoterpenes, oleoresin is composed of volatile sesquiterpenes and non-volatile diterpene acids. The composition and quantity of wood oleoresin depends on e.g. tree species, age, provenance, health status, and environmental conditions (Back and Ekman, 2000, Erbilgin and Colgan, 2012), and is likely linked to protection against stem-damaging herbivores (Lewinsohn et al., 1991; Philips and Croteau, 1999; Trapp and Croteau, 2001). Oleoresin flows out from a mechanically damaged site to protect the tree by sealing the wound. Once in contact with air, the volatile parts of oleoresin evaporate, and the residual compounds harden to make a solid protective seal over damaged tissues. Yet, a fraction of volatile part may react already on the oleoresin and form large polymers of low volatility.

It is well known that also the foliage of conifers contains several volatile isoprenoids (isoprene, monoterpenes, sesquiterpenes), as well as small oxygenated carbonyls, e.g. methanol, acetone and acetaldehyde, which are emitted at very variable rates (e.g. Isidorov et al., 1985; Christensen et al., 2000; Grabmer et al., 2004). Temperature is the main controlling factor for monoterpene emission, influencing their volatility in an exponential manner (Tingey et al., 1980), although recently light-dependent emissions from shoots have also been reported (Loreto et al., 1996; Staudt and Bertin, 1998; Shao et al., 2001; Tarvainen et al., 2005; Ghirardo et al., 2010), indicating a close dependence with carbon assimilation. Emissions of monoterpenes from tree canopies have a typical seasonal pattern, normally peaking in summer (e.g. Hakola et al., 2006).

Surprisingly, despite abundant knowledge on emissions of volatile isoprenoids from foliage, very little is known about their emissions from woody plant tissue. From the viewpoint of the timber and paper industry, isoprenoid emissions from harvested and further-processed timber have been previously reported (Strömvall and Petersson, 1991; 1993; Granström, 2007), but living woody tree parts have gained only little attention. As the oleoresin storage pools in stems are large, emissions occur constitutively without any damage to the tree itself, but their seasonal patterns or driving factors have not been studied in detail.

Resin duct network and water transport system are both pressurized systems: resin is under positive pressure caused by cells surrounding the ducts and xylem water under negative pressure caused by the transpiration created tension linking the pressure to many physiological processes of a tree. Apart from transpiration the water status in stem is linked to repeated freezing and thawing cycles in winter. These can cause embolism in water conducting tracheids (Sperry, 1993) potentially hindering the stem water transport as transpiration commences at spring recovery of the canopy. Thus one requirement for trees living in cold environments is that the xylem conduits are refilled and the water transport capacity recovers in the spring (e.g. Améglio et al., 2002). The water pressure changes in xylem and phloem can be reflected to the radial changes of inner-bark and xylem (e.g. Mencuccini et al., 2013)

Interestingly, emissions from intact Scots pine branches can be very high in early spring, in many cases much higher than those later in the growing season (e.g. Tarvainen et al., 2005; Hakola et al., 2006). This implies that other factors, related to the tree physiological processes in spring may also influence inherent emission rates, beyond the simple physical factors related to volatilization of VOCs or the~~.~~ factors related to biotic or abiotic damage.

To analyze the dynamics of stem monoterpene emissions and their possible relationship to the stem physiology in spring, we measured the emissions from a Scots pine stem during two springs in field conditions in a boreal pine forest. In addition, we measured sap flow, stem radial variation and foliage~~leaf~~ gas exchange (including emissions of monoterpenes) from the same tree. Our hypothesis was that the emissions from the stem are driven by several factors: one is related to incident changes in temperature (affecting volatilization), ~~and solar radiation~~ and the second one represents the ~~storage~~ dynamic emission ~~from different parts of the tree~~driven by tree physiological processes. The latter one wa~~i~~s expected to be linked to tree water relations, and thus the onset of monoterpene emissions from the stem in spring ~~is~~ could be related to the recovery of tree water transport capacity.~~ This can be characterized with dynamics in sap flow, transpiration and pressure changes in stem as reflected in its diameter variation.~~

2 Materials and methods

Measurements were done at the SMEAR II (Station for Measuring Forest Ecosystem–Atmosphere Relations, 61°51’N, 24°17’E) stand (Hari and Kulmala, 2005) in 2012 and 2013.

The growing season ~~there~~ ranges, on average, from the end of April to mid-October (Table 1). Thermal spring, defined as a period when daily mean temperature stays between 0 and 10 °C, starts typically during the first half of April (Table 1). ~~-~~The ~~start of the~~ growing season ~~takes place~~starts when snow has melted on open sites and mean daily air temperature rises above 5 °C~~. At our measurement site~~, this takes place around the turn from April to May. The ambient air temperature, snow depth and soil water content during the measurement periods in April–May 2012 and 2013 are shown in Figure 1.

The measurement site is situated at the boreal vegetation zone in southern Finland. The stand is dominated by Scots pine with some Norway spruce (*Picea abies* (L.) Karst.), European aspen (*Populus tremula* L.), and birches (*Betula* spp.) as a mixture. The ground is covered with dwarf shrubs (*Vaccinium myrtillus* L., *Vaccinium vitis-idaea* L.) and mosses (*Pleurozium schreberi* (Brid.) Mitt., *Dicranum* spp.). Soil is haplic podzol formed from glacial till and its thickness on bedrock is quite low, on average only 0.5–0.7 m.

The tree-scale parameters were measured from a visibly healthy, representative Scots pine ca. 50-yr old individual belonging to the dominating canopy layer. This tree was 18.6 m tall and had a diameter of 20 cm at breast height (in 2012), and has been measured for diameter change and sap flow since 2005. The lowest living branches grew at a height of 10 m. The shoots and stem were inspected visually, and no injuries or other abnormalities could be seen before or after the installation of measurement device.

The gas exchange of the stem was measured with a transparent enclosure (see below). The flux calculation of stem enclosure data was done according to Kolari et al. (2009). The top-canopy shoot gas exchange was measured at the height of about 17 m with a dynamic enclosure (including 2–3 most recent needle year classes) as presented by Aalto et al. (2014). The shoot gas exchange was calculated as in Kolari et al. (2012) with a transpiration correction as in Altimir et al. (2006). Until the end of April 2013 the H_2O and CO_2 exchange was measured with URAS 4 infrared light absorption gas analysers (Hartman and Braun, Frankfurt am Main, Germany), and from May 2013 onwards with a Li-840A analyser (Li-Cor, Lincoln, NE, USA). The replacement of the gas analysers did not cause any irregularity in the H_2O and CO_2 exchange data because the calculation of gas exchange is primarily dependent on concentration difference instead of absolute concentration, and besides of that both analysers were also calibrated for CO_2 using comparable calibration method and standard gases containing ca. ambient concentration of CO_2. For more details on CO_2 and

H_2O calibration protocol used at SMEAR II, see Keronen et al. (2014). ~~The replacement of the gas analysers did not cause any irregularity in the measurement data.~~ The stem CO_2 efflux was temperature-normalised using the air temperatures measured inside the enclosure to study linkages with other stem processes by fitting an exponential curve to measurements at above zero temperatures in April. S~~The s~~imple exponential models derived from the described plot (Eqs 1, 2) were~~as~~ then used to estimate CO_2 efflux anomalies. The exponential models for respiration (R) as a function of ambient temperature (T) were

$$R = 4.5784 * \exp(0.0925 * T) \quad \text{(Eq 1)}$$

and

$$R = 0.9874 * \exp(0.207 * T) \quad \text{(Eq 2)}$$

for April 2012 and April 2013, respectively. ~~.~~

The VOC emissions were measured online with a proton transfer reaction-quadrupole mass spectrometer (PTR-Q-MS, Ionicon, Innsbruck, Austria; Hansel et al., 1995) modified from the system described in Ruuskanen et al. (2005). The description and accuracy of the VOC measurement system has been reported in Kolari et al. (2012). Altogether, ten protonated mass ions ~~molecular masses~~ (amu+1) were monitored~~) were measured~~, but for this study we use data only on the m/z 137, which corresponds in Scots pine emissions mainly to monoterpenes. The other masses show so low signal-to-noise ratios and dependence on air humidity that their fluxes are insufficiently quantified. Calibrations of the PTR-Q-MS were carried out 2–3 times a month according to the method described in Taipale et al. (2008)~~,~~ ~~including α-pinene as the representative monoterpene~~. A mixture of several VOCs (e.g. α-pinene as a representative of monoterpenes) in nitrogen was used as a gas standard. The mixture was further diluted with volatile-free air from a zero air generator to attain concentrations below 20 parts per billion by volume, i.e. around the ambient atmospheric concentrations. The ~~other~~ gaps in the data originate from the momentary maintenance and malfunction of the measuring system. As the temperature variation in springtime is wide, the measured emissions were normalized to enable better comparison by applying the

temperature normalization equation according to Guenther (1997) using an empirical beta-coefficient of 0.09 ~~°C~~K^{-1} and a standard temperature of ~~30 °C~~303.15 K according to Eq (3). ~~All the monoterpene emissions from the stem are expressed per m^2 of bark area and the emissions from the shoot per m^2 of all-sided needle area. The stem area was defined as a smooth cylinder surface ignoring the cracks of the bark.~~

$$E_0 = E * \exp(\beta * [T_S - T]) \quad (3)$$

where E_0 = normalized emission rate (ng m^{-2} s^{-1}), E = observed emission (ng m^{-2} s^{-1}), β = 0.09 (°K^{-1}), T_S = standard temperature (K), and T = temperature in chamber (K).

The stem enclosure (Figure 2) was designed specifically for ~~this purpose~~measuring reactive gases with materials chemically inert to many VOCs to avoid detrimental signal losses. The enclosure covered 396 cm^2 of the pine stem at the height of 12 m from the ground, which is close to the lowest living branches. The enclosure consists of a transparent and UV-permeable FEP foil (0.05 mm thick, Fluorplast, Maalahti, Finland) wrapped around the stem 2–3 times and tightened with binds on both ends. The vertical seal of the foil was made with FEP tape. Within the enclosure, a spiral of polyethylene-coated aluminium tube (Synflex, Eaton, USA) was wrapped around the stem to maintain an air space between the foil and the bark, and a FEP tape-covered aluminium brace for inlet and outlet connectors was placed between the spiral and the foil. Inside the enclosure, temperature was recorded with a copper-constantan thermocouple on the south-facing side of the stem. Rain water flow along the stem was blocked with a rain cover above the enclosure. Mounting of the enclosure was done well before the first measurements and without damaging the bark to avoid possible induced emissions. The bark at this height was rather smooth, so no levelling with a knife was needed. The measurements were done in steady state when the flow rate through the enclosure was about 1 l min^{-1}. The sampling time for emissions was 2 min 45 s, and samples were taken 24 times per day. To avoid accumulation of gases inside the enclosure, the enclosure was flushed between the samplings with above-canopy air at a rate of about 0.4 l min^{-1}. All the monoterpene emissions from the stem are expressed per m^2 of bark area and the emissions from the shoot per m^2 of all-sided needle area. The stem area was defined as a smooth cylinder surface ignoring the cracks of the bark.

Changes in stem radius were measured with two linear variable displacement transducers (point-dendrometers) (LVDT; model AX/5.0/S, Solartron Inc. West Sussex, U.K.), at a height

of 15 m from the base of the sample tree. The point-dendrometers were installed to a rectangular stainless steel frame and were affixed onto the stem using two attachment plates. A detailed description of the dendrometers is provided by Sevanto et al. (2005). The head of the first dendrometer rested against a screw that was placed 10 mm through the bark surface, measuring xylem radial thickness (d_x). The head of the second dendrometer rested against the inner-bark, which was exposed by incising the outer-bark 3–4 mm deep with a scalpel. This dendrometer measured whole stem radial thickness (d_{ws}). As whole stem thickness also includes xylem thickness, the difference between these measurements is the inner-bark radial thickness (d_b). Inner-bark thickness, hence, includes the cambium and the phloem tissue towards the outside of the cambium. Dendrometer measurements (accuracy 1 µm) at 30 minute intervals were used for the study and were offset to zero on April 1 of each year.

We used the radial measurements to calculate a dimensionless ratio, β, which is the ratio of the change in d_x to the change in d_b (Eq 4):

$$\beta = \frac{d_{b\mathrm{MAX}} - d_{b\mathrm{MIN}}}{d_{x\mathrm{MAX}} - d_{x\mathrm{MIN}}} \qquad (\text{~~1~~}4)$$

where $d_{b\mathrm{MAX}}$ and $d_{b\mathrm{MIN}}$ correspond to the maximum and minimum daily inner-bark diameter, respectively, and $d_{x\mathrm{MAX}}$ and $d_{x\mathrm{MIN}}$ corresponded to the maximum and minimum daily xylem diameter, respectively. This ratio is proportional to the ratio of the elasticity of the inner-bark tissues to xylem tissues. Note that an assumption is made here that the xylem and inner-bark tend towards water potential equilibrium with each other at the minimum and maximum diameters. As the elasticity of the xylem tissue is dependent mainly on the elastic properties of the dead xylem tracheids (Irvine and Grace, 1997; Perämäki et al., 2001) and the xylem and inner-bark (Sevanto et al., 2011) tend to approximately follow water potential equilibrium on a daily scale, the changes in β represent mainly the changes in the elasticity of the phloem.

Sap flow rate was measured with the Granier-type heat dissipation method at a height of about 13 m. Two probes, of 50 mm in length, were inserted in 2 mm wide brass cylinders into the sapwood approximately 10 cm apart. The upper probe (with 30 ohms resistance) was heated with constant power (approximately 0.2 W) and the sap flux density was calculated from the temperature difference between the two probes with a standard protocol (see e.g. Granier, 1987).

Air temperature was measured at 8 m height (Pt-100 sensor) and in soil A-horizon (5–10 cm depth with Philips thermistors). Precipitation was measured (Vector ARG-100 tipping bucket rain gauge and Vaisala FD12P Weather sensor) in an open site at 30-min intervals. Snow depth was measured once a week at seven locations below canopies at the study site and averaged for the forest stand.

3 Results

Weather patterns in both springs were rather normal (Table 1). Mean temperatures in April were somewhat below the long-time average, but May temperatures were slightly higher. The onset of the growing period was typical for the site. The maximum depth of snow was in both years higher than average, but snow was melting slightly earlier than normal.

The emission measurements show that very early in spring, already in early April, significant monoterpene emissions from pine stem and shoot could be detected (Figure 3). The emissions exhibited a clear diurnal cycle, with a maximum at midday and a minimum at midnight (Figure 3a, b). Interestingly, a single, extremely high burst of monoterpene emission was observed from the stem on both years in April. At highest, the monoterpene burst was 13 ng m^{-2} s^{-1} in 2012 and 50 ng m^{-2} s^{-1} in 2013. The corresponding normalized (30°C) emissions in the bursts were 77 ng m^{-2} s^{-1} and 500 ng m^{-2} s^{-1}, respectively. In 2012, the peak occurred on 11 April, when the mean air temperature was 3.6 °C, and in 2013 on 19 April when the mean air temperature was 3.4 °C. The average, temperature normalized emission rate from the stem was 29 µg m^{-2} day^{-1} after the burst in April–May 2012. In 2013, the normalized emission rates were 79 µg m^{-2} day^{-1} before the burst in April and 47 µg m^{-2} day^{-1} after the burst in April–May, respectively. In 2013, the mean measured monoterpene emission from the stem in April before the burst was 0.7 ng m^{-2} s^{-1} (standard deviation 0.6 ng m^{-2} s^{-1}) and after the burst in April–May1.3 ng m^{-2} s^{-1} (standard deviation 1.5 ng m^{-2} s^{-1}).

The transient~~.~~ extremely high monoterpene emissions occurred after the freeze-thaw cycles, but their timing was different from the pre- and post-peak periods and –varied slightly between years: in 2012, the highest values were measured in the afternoon, around 15:00, whereas in 2013 the highest values occurred in late evening, around 21:00 (Fig ~~5~~ 4a, b). In 2012, the high emissions were recorded for 12 hours, after which, emissions returned to their normal, low levels. In 2013, the emission measurements were unfortunately interrupted due to

a communication error between the PTR-MS and the laptop controlling it during the peak emission. Before the break, the high emissions had continued for nine hours.

The stem monoterpene emission peaks in April were not coinciding with the highest emission periods from shoots (Figure 3). The stem and shoot monoterpene emissions were momentarily at about the same level during the stem monoterpene burst in 2012, but in 2013, the stem monoterpene emissions clearly exceeded those from the shoots. ~~Both the needles and the stem looked viable and no injuries or other abnormalities could be seen.~~

The observed inner-bark radial thickness (d_b) dynamics were very different before, during and after the observed emission burst. Thus, we separated them into three consecutive phases. The first phase began in early April, when large and reversible stem swelling and shrinkage was observed, which was associated with repeated freeze-thaw cycles (Figures 4 and 5). These freeze-thaw cycles were observed over the first nine days of both Aprils, coinciding with daily minimum temperatures below –5ºC.

The second phase began once monoterpene emission started. Immediately after the stem monoterpene emission burst ceased, a~~n acclimation response~~ period lasting roughly one week was seen in d_b (Figure ~~4A~~5a, b~~, B~~). Recovery of the d_b from the first period's freeze thaw cycles was detected, which occurred roughly three days after the burst in 2012 and almost immediately in 2013. On the 11–23 April 2012 and 19–25 April 2013, d_b and d_x were swelling and shrinking with no time lag, or even d_b swelling occurring before d_x. We considered the end of the second phase to take place once the d_x and d_b changes got more regular. Thus, the stem and its water transport got acclimated to external factors such as rising air temperature.

In the third phase, a regular swelling and shrinking of stem radius was observed: d_b followed d_x with a time lag ~~of approximately 30–60 minutes~~. This kind of pattern is typical for the active growing period and is commonly observed in summertime at the study site. Moreover, irreversible d_b increment (i.e. radial growth) began shortly after the second phase.

Sap flow decreased and minimum occurred ~~consistantly~~ about 10 days after the peaks in monoterpene emissions, and then began to increase steadily to summertime levels following similar pattern in temperature (Figure 6). Nighttime sap flow occurred concurrently with the stem monoterpene emission peaks (Figure ~~5~~4), which does not typically occur at any other time of the year at this site. In addition, shoot transpiration was very low during 2012 emission peak, although VPD was high, indicating closed stomata (data not shown).

β, reflecting the changes of inner-bark to xylem maximum daily amplitude showed large daily variations prior to the emission burst followed by a decline shortly after (Figure 7). During the second phase, β exhibited noticeably smaller but abrupt changes lasting 2–3 days. After this response period, β reached a steady summer state.

The stem CO_2 efflux anomalies, i.e. the part of respiration value that is not explained by the regular response to temperature (Figure 8), reveal that prior to the high monoterpene emission peak of both years, the stem CO_2 efflux anomaly increased relative to period before, or immediately after in 2012 (2013 measurements were missing at that period due to system problems). This suggests that in addition to regular maintenance respiration, CO_2 was released from some storage or there were some CO_2-producing processes occurring. This high CO_2 efflux during the monoterpene peak is not associated with growth since radial growth was observed with the point dendrometers approximately one month later.

4 Discussion

We showed that in a boreal forest, monoterpenes are emitted from Scots pine stems continuously at a low rate in spring, with a systematic daily pattern – maxima in the afternoon and minima during night-time. The stem monoterpene emissions differ from those measured from shoots in both magnitude and dynamics at the same time. The monoterpene emission from Scots pine shoots show clear seasonal pattern with several high transient emission periods in the beginning of the growing season (Aalto et al., 2014). The average level of the monoterpene emissions from the stem in springtime ~~are~~ is in general lower than from the shoots (per area unit), which is likely due to lower oleoresin content and lower biological activity in stem than in shoot (Rockwood, 1973; Back and Ekman, 2000). The monoterpene emissions from the shoot were generally lower in 2013 than in 2012 (Figure 3), but this is likely due to the aging of needles as the same shoot was enclosed in the measurement chamber in both years (Aalto et al., 2014). Moreover, the dynamics of the monoterpene emissions from the stem and shoots seem to be driven by different factors.

We compared the fluxes measured with chambers to those monitored with ecosystem scale flux measurements (data not shown), but no clear correlations could be seen. Since the ecosystem scale measurements upscale the emissions of the whole heterogenic stand, such transient physiological features related to emission changes in individual trees may not be observable at that scale. As the environmental factors vary within a forest stand and the tree

individuals exhibit naturally somewhat different responses to these factors, there is variance in timing of the physiological processes within a stand.

In addition to the continuous low monoterpene emissions from the stem, we observed a rapid but large emission burst, lasting for several hours, after which the emissions decreased to the pre-burst levels, with a gradual emission increase towards summer concurrently with increasing ambient temperatures. The monoterpene emission burst coincided well with the recovery of stem radius from winter conditions. In both years studied, the burst occurred shortly after the last freezing period (Figure ~~4~~5). Around the time of the burst, stem radius fluctuations showed irregular behaviour in comparison to the regular pattern observed during summer condition, more noticeably in 2012. This behaviour included inner-bark fluctuations occurring before xylem fluctuations, both inner-bark and xylem changes occurring concomitantly and large daily fluctuations unlike summer-time behaviour. In both years, the inner-bark radius had a depression relative to xylem around the emission burst, but extremely so during 2012. This behaviour also coincided well with the changes in relative bark-xylem daily amplitude, β, where the largest changes were seen shortly before the burst (Figure 7) and also more prominent in the year 2012 when the bark shrinking was more pronounced. Also the dynamics of sap flow behaved in similar manner relative to the burst event on both years (Figure 6). This irregular behaviour ~~in both~~ relative to timing~~, degree of swelling~~ and ~~relative~~ amplitudes of xylem and inner-bark indicates that other driving forces than transpiration, the main driver of diameter change variation during summer (Perämäki et al., 2001; 2005),~~than during the regular diameter variation in summer when transpiration pull~~ drives the pattern ~~-~~of diameter change variation. ~~(Perämäki et al., 2001; 2005)~~.

It is commonly known that ~~The~~ freeze/thaw cycles experienced during winter cause winter embolism in trees ((Sperry, 1993; Sperry and Robson, 2001~~;~~ Pittermann and Sperry, 2006)): frozen gases (mostly air and CO_2) dissolve in xylem sap forming bubbles, which then expand during thawing and ~~embolise~~ embolize the water conducting tracheids~~ (Sperry, 1993; Pittermann and Sperry, 2006)~~. In spring, xylem conduits are refilled with water by metabolic processes which are not yet fully understood, but most likely involve the interaction of living cells and radial interaction between xylem and phloem (Zwienieki and Holbrook, 2009; Nardini et al., 2011), resulting in the recovery of xylem transport capacity along with transpiration-driven tension propagation in stems. Cochard et al. (2001) demonstrated that an active mechanism for the recovery of shoot hydraulic conductivity via embolism refilling

occurred early in the growing season, before cambial reactivation (i.e., before ring development). Also aquaporin activity, which changes the permeability of the cell membranes, is known to be associated with embolism refilling (e.g. Sakr et al., 2003; Brodersen and McElrone, 2013).

Studies have shown that the inner-bark (i.e. phloem), plays a contributory role by providing the mechanism to drive radial water flow, ultimately aiding osmotic flow into ~~embolised~~ embolized conduits (Salleo et al., 1996; Zwieniecki et al., 2000; Salleo et al., 2004). Also our results show that soon after the cessation of freeze-thaw events there occur changes, such as temporary shrinking of inner-bark relative to xylem and high inner-bark vs. xylem amplitude changes, which could suggest an active role of phloem in xylem recovery. Also the stem CO_2 flux anomalies might be related to this phloem activity during embolism refilling as embolism refilling is known to require input of energy (Zwieniecki and Holbrook, 2009). After this period, changes in stem radius achieved a general summer-time steady state, where changes in inner-bark follow xylem changes with a 30–45 min time lag (Sevanto et al., 2002). ~~Also the sap flow rate starts to increase after this recovery period (Figure 6), which indicates the initiation of tree growth.~~

The simultaneous dynamic changes in stem radius and deviation of xylem sap flow from normal conditions indicate that the changes in stem water relations are at least coinciding if not causing the emission bursts in April. ~~Alternatively~~In addition to water transport, the shrinking and swelling of phloem could indicate the onset of growth: xylem microcore samples have indicated that xylem cells start forming at our measurement site after mid-May (Jyske et al., 2014) and phloem cells have been reported to start to form about 10 to 20 days before xylem cells in Scots pine (Antonova and Stasova, 2006). Thus, the timing of tree growth does not explain the observed bursts which were seen to occur prior to growth onset, and we need to search for explanations from other physical and physiological processes.

~~The of new phloem cells and the collapse of the old ones as phloem cells have been reported to start to form about 10 to 20 days before xylem cells in Scots pine (Antonova and Stasova, 2006). Furthermore, xylem microcore samples have indicated that xylem cells start forming at our measurement site after mid-May (Jyske et al., 2014). Thus, the~~ The most potential~~plausible reasons~~causes for these transient monoterpene bursts from pine stem ~~are~~ are~~1)~~ volatilization from storages due to temperature increase (e.g. Lerdau et al., 1997~~, …~~); ~~2)~~ changes in the non-

specific storage of monoterpenes (e.g. Niinemets and& Reichstein, 2002); and or 3) a rapid pressure-induced mobilization of volatiles from resin ducts in shrinking xylem tissue.

As volatile cues are important for many herbivores in finding their host trees, the springtime monoterpene emission dynamics may also be linked to tree-herbivore relations. We will discuss the three points in the following sections.

4.1 Direct e Effect of temperature

Monoterpene volatilization is a temperature-driven process (Guenther et al., 1993; Guenther, 1997; Lerdau et al., 1997; Tarvainen et al., 2005) and thus the seasonality of monoterpene emissions from vegetation is often linked to changes in ambient temperatures. Temperature-dependent emissions are especially important in species with large storage pools, such as conifers (e.g. Lewinsohn et al., 1991; Lerdau et al., 1997). The accumulation of monoterpenes in stem storage pools over winter and their release due to higher temperatures in spring could possibly lead to high emission rates. However, the temperatures at the day of the burst were not by any means higher than in spring on average: in 2012 the maximum temperature was 10 °C and in 2013 8 °C. In 2012 it was the warmest day until that date, but in 2013 there was somewhat warmer day three days before. Wwe could not identify any extraordinary weather conditions which could have caused such high emission peak. No anomalous temperatures for the season were detected, neither any other unusual environmental factors. The emission burst had on both years almost similar timing compared to the growing season: the growing season started on 12 April 2012 and 16 April 2013. The burst took place on 11 April in 2012 and on 19 April in 2013 (onset of growing season 12 April and 16 April, respectively). Also the daily mean temperatures of the peak emissions days were almost identical in both years.

The bark surface temperature follows ambient air temperature with a short time lag, but may occasionally rise well above ambient temperature due to direct irradiation on the bark surface. However, inside and especially below the canopy this happens only occasionally and only on one side of the stem at a time, and especially . Furthermore, deeper inside the stem the response to changes in ambient temperatures is very slow. Measurements on a 60 cm thick Monterey pine have shown that diurnal temperature range inside the stem is only about one third of the range in ambient air (Neher, 1993). Thus, the oleoresin-rich heartwood (Strömvall and Petersson, 2000) stays in more stable conditions than the sapwood with lower oleoresin

content. On the other hand, sapwood includes the living cells of the xylem and thus its temperature changes might be more significant for monoterpene emissions, especially in the case of de novo emissions. Our stem enclosure was situated inside the living canopy, so there apparently was only living sapwood and no heartwood enclosed.

It is also possible that the monoterpenes get reallocated from roots to upper tree parts through sap flow. However, as oleoresin is still rather viscous at that the prevailing temperatures in spring, and the monoterpenes do not easily dissolve to water, this may not provide a good explanation for the observed peak emissions.

~~Niinemets and Reichstein (2003a,b) concluded that the physico-chemical and structural factors explain well the shoot emission bursts of water-soluble VOCs such as methanol (with rather low Henry's law constant, H) when stomata open in the morning. On the other hand, fast temporal kinetics and liquid/gas phase transfer is reasonably irrelevant for compounds such as monoterpenes with rather large Henry's law constants, which generally have gas and liquid phase pools in a steady state. Thus, direct temperature effect is not capable to explain the bursts.~~

4.2 Changes in non-specific storage of monoterpenes due to changes in membrane permeability during spring

~~Monoterpenes are lipophilic and a dynamic, non-specific storage pool exists in cellular membranes (Niinemets and Reichstein, 2002; 2003; Ormeño et al., 2011). This pool may either influence or be affected by membrane permeability changes. At high concentrations monoterpenes may alter the properties of membrane proteins (Wink, 2003) and thus also affect the permeability and other bioactive features of the membrane. It has been suggested that monoterpenes affect membrane permeability and may cause leakage of intracellular materials of pathogenic microbes, which could explain their antimicrobial activity (Trombetta et al., 2005; Cristani et al., 2007).~~

~~Parallel to xylem refilling described above, t~~The spring dehardening ~~process of symplasm during spring~~ involves many biochemical changes affecting membrane transport properties and~~,~~ ~~e.g. the decrease in phospholipid content and biophysical changes of the membranes,~~ changing membrane permeability (Pukacki and Kaminska-Rozek, 2013; Martz et al., 2006), which likely also influence~~s~~ the water relations ~~between symplasm and apoplasm~~ in stem~~,~~ and

~~hence, also~~ xylem refilling. ~~It is likely that c~~Changes in membrane properties (e.g. elasticity and permeability) were likely seen~~, in our case,~~ as changes in stem radius measured with point dendrometers. The change in permeability is reflected in the water status of the living cells of the stem, affecting sap flow rate as well.

A dynamic, non-specific monoterpene storage pool exists in cellular membranes (Niinemets and Reichstein, 2002; 2003; Ormeño et al., 2011). This pool may either influence or be affected by membrane permeability changes. At high concentrations monoterpenes may alter the properties of membrane proteins (Wink, 2003) and thus also affect the permeability and other bioactive features of the membrane. Monoterpenes may affect membrane permeability and cause leakage of intracellular materials of pathogenic microbes, which could explain their antimicrobial activity (Trombetta et al., 2005; Cristani et al., 2007). ~~It is possible that the~~Since the properties of ~~the~~ cell membranes ~~in xylem and phloem tissues~~ change~~d~~ dramatically du~~e to~~ ring dehardening, this may lead~~ing~~ to a release of membrane-accumulated monoterpenes – however it is unlikely that the release would be seen as such a short and transient emission peak, but rather as a gradually increasing emission rate as the dehardening proceeds.

~~The change in permeability is also reflected to the water status of the living cells of the stem, which may have caused the changes in sap flow rate as well. On the other hand, if the irregular inner-bark dynamics were associated with the collapse of previous years phloem associated with new phloem growth, then the monoterpene burst may originate from storages in there.~~

4.3 A rapid mobilization of volatiles from resin ducts

A rather plausible explanation for the monoterpene emission peaks is a pressure-induced release of volatiles from resin duct cavities. Resin ducts are located both horizontally and vertically in the stem, and thus they are in contact with both heartwood and sapwood. ~~Based on our measurements, it is impossible to conclude from which stem tissues (e.g. tracheid cells, resin ducts, bark etc.) the observed monoterpenes originate. It is likely that t~~The ~~spring-induced~~ rapid changes in water transport and related pressure changes in stem in spring could ~~potentially be~~ lead~~ing~~ to a pressure change in the xylem resin ducts and a consequent release of oleoresin. Such an effect could be corresponding to a damage-induced, transient release of monoterpenes from herbivory or mechanical wounding. However, after a steady diurnal water transport rate is obtained (in some hours after the recovery of the xylem), the resin ducts are

no longer experiencing strong pressure effects and emissions go down to 'normal' diurnal pattern.

~~One more possibility could be that m~~Monoterpene emissions may also originate from the gases inside ~~embolised~~ embolized tracheids. It is well known that a~~A~~ large proportion of tracheids is ~~embolised~~ embolized ~~after~~ during the winter as gas bubbles get trapped inside the frozen xylem sap during freezing and expand to ~~embolise~~ embolize the tracheids during thawing (e.g. Pittermann and Sperry, 2003). ~~Supposedly T~~the air inside the ~~embolised~~ embolized tracheids ~~has~~ may have a high concentration of monoterpenes, as the turnover rate of the gases is low and ~~there is ample time for the~~ monoterpenes ~~to~~ can diffuse to tracheids from the neighbouring resin ducts ~~and plasma membranes~~over the winter. Once the conduits refill with water in the spring, the gases, including monoterpenes, within the ~~embolised~~ embolized tracheids diffuse out from the stem (Yang and Tyree, 1992; Vesala et al., 2003). It is unclear how large are the changes in stem gas content during the spring ~~at our site~~, and if monoterpene concentrations can ~~get~~ be high enough to sustain a burst for several hours. However, substantial changes in the volume of gas inside the stem are very likely, as the volumetric water content of the stem is known to vary a lot during winter months (Sparks et al., 2001) and can increase by up to tens of percent's during the springtime (Wullschleger et al., 1996).

~~Yet, an explanation could be that~~On the other hand, o~~o~~nce the ~~embolised~~ embolized tracheid cells fill up with water in spring, the filling causes extra pressure on resin ducts and this may also cause~~s~~ micro-scale damages on the ducts ~~and the~~ followed by a subsequent oleoresin flow ~~is seen as~~and elevated monoterpene emissions. ~~In this case the damages would be so remarkable that they release volatiles, but so small that they are not visible on the bark surface.~~

5 Conclusions

A~~The irregular diurnal pattern of stem radial change compared to summer conditions, as well as night-time sap flow, accompanied by low shoot transpiration rates during the monoterpene burst was observed in two consecutive years. We also detected a difference in the ratio of the daily amplitude of phloem to xylem radial thickness and/or osmotically driven swelling~~

~~before and after the burst. These dynamic changes indicate a phase change in stem water transport capacity that precedes the physiologically active summer state of the tree. The measurements show that there was a water transport acclimation period of a few days after the monoterpene burst occurred. After this period, the water transport capacity reached a steady summer state and daily patterns of stem radial change and sap flow rate stabilized. This suggests that there is a significant mechanism involved in the described physiological process. The spring-time as well as other phenological responses of woody plant parts to environmental drivers have been discussed recently by Delpierre et al. (2015).~~

~~This study is the first to show that monoterpene emissions from Scots pine stems are linked to changes in stem water relations during the spring recovery, indicated by sudden changes in stem radius and disruption of the normal diurnal cycle of xylem sap flow during the highest emission burst. The stem emissions are in general much lower than those from green plant parts, but our study indicates that the mechanisms related to stem emissions are less related to changes in environmental conditions than to the physiology of the tree, especially during the winter dehardening phase. The results open interesting new insights on the measurements of monoterpene emissions: a~~lthough emission measurements on tree shoots using branch enclosures abound, ~~we know practically~~ very little is known ~~of~~ on the ~~detailed~~ emission patterns and their driving factors of the woody parts of the shoots~~, which may be very different than in leaves or needles.~~This study is the first to show that monoterpene emissions from Scots pine stems are linked to changes in stem water relations during the spring recovery. The stem emissions seem to be less related to changes in incident changes in environment than to the physiology of the tree, especially during the winter dehardening phase. The dynamic changes in stem processes (irregular diurnal pattern of stem radial change, night-time sap flow, and transient monoterpene burst) indicate a spring-time phase change in stem water transport capacity that precedes the physiologically active summer state of the tree. After this period, the water transport capacity reaches a steady summer state with stable daily patterns of stem radial change and sap flow rates. While t~~T~~he emission dynamics in ~~leaves~~foliage ~~may~~ follows ~~the traditional~~a clear temperature ~~(pools)~~ and light ~~(synthesis)~~ dynamics~~responses~~, ~~but in woody compartments~~ the large oleoresin reservoirs in woody compartments seem to be ~~are~~ less directly affected by these incident factors, and rather ~~more likely~~ reflecting a longer term adjustment of the whole tree physiology. The large transient emission peaks from stem are most likely related to the springtime refilling of embolized tracheids. ~~Furthermore, the f~~Future ~~directions on~~studies on the topic ~~should~~ could address the

~~studies on~~ cellular-level processes in tree stems, and their connections to seasonal water transport capacity and occurrence of insect outbreaks.

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Table 1. Environmental variables at the study site during statistical period 1981–2010 and in studied years 2012 and 2013.

	1981–2010 [1)]	2012 [2)]	2013 [2)]
Annual mean air temperature, °C	3.5	3.3	4.9
Minimum air temperature, °C	–38.1 (January 1987)	–31.7 (4 February)	–29.5 (18 January)
Maximum air temperature, °C	33.1 (July 2010)	27.5 (29 July)	29.6 (26 June)
Annual precipitation, mm	711	907	615
Annual maximum snow depth, cm	43	76	68
Duration of snow cover, days	227	157	179
First snow [3)]	15 October	28 November	26 October
Snow melt	15–30 May	4 May	24 April
Thermal spring start	5 April	10 April	12 April
Start of the growing season	27 April–2 May	25 April	27 April
Annual cumulative temperature sum, degreedays	1200–1300	1161	1388
April mean temperature, °C	2.3	1.5	1.7
April minimum temperature, °C	–19.7	–16.5	–14.5
April maximum temperature, °C	23.4	13.9	11.9
April precipitation, mm	37	60	42
May mean temperature, °C	8.9	9.4	12.2
May minimum temperature, °C	–7.1	–2.9	–2.7
May maximum temperature, °C	28.2	23.8	24.9
May precipitation, mm	45	56	16

[1)] Statistical data for years 1981–2010 is collected from Pirinen et al. (2012) and from Finnish Meteorological Institute (FMI) webpages (2014). [2)] Data from FMI open access data. [3)] Date in the previous year.

Figure legends

Figure 1. A–B. Temperature at 8.4 m in air and in soil A horizon (°C). C–D. Weekly snow depth (cm) and volumetric soil water content in A horizon (m^3 m^{-3}). Left-hand panels are for April–May 2012 and right-hand panels for April–May 2013.

Figure 2. The stem enclosure around a Scots pine stem at a height of 12 m (left) and a linear variable displacement transducer to measure stem radius changes (right).

Figure 3. A–B. Measured monoterpene emission (m/z 137, ng m^{-2} bark area s^{-1}) from the pine stem (same location on the stem in both years). C–D. Measured monoterpene emission (m/z 137, ng m^{-2} total needle area s^{-1}) from a pine shoot (same shoot in both years).– E–F. Temperature (°C) in the stem enclosure. Left-hand panels for April–May 2012, right-hand panels for April–May 2013.

Figure 4. A–B. Monoterpene emission from the stem (m/z 137, ng m^{-2} bark area s^{-1}) and the air temperature (°C) inside the enclosure. C–D. Stem sap flow (kg h^{-1}) and inner-bark and xylem radius (µm). Left-hand panels for April 2012 and right-hand panels for April 2013. The grey shading refers to the periods when the stem was frozen. The timing of the monoterpene burst is marked with dotted lines in the lower panels.

Figure ~~4~~5. A–B. Pine stem xylem and inner-bark radius changes (µm). C–D. Stem sap flow (kg day^{-1}). E–F. Vapor pressure deficit (VPD, Pa). Left-hand panels for April 2012 and right-hand panels for 2013. The grey shading refers to the periods when the stem was frozen. The timing of the monoterpene burst is marked with dotted lines. A closer look on the burst period is provided in the Figure ~~5~~4. The Roman numerals refer to the three phases of inner-bark radial changes discussed in the text.

~~Figure 5. A–B. Monoterpene emission from the stem (m/z 137, ng m^{-2} bark area s^{-1}) and the air temperature (°C) inside the enclosure. C–D. Stem sap flow (kg h^{-1}) and inner-bark and xylem radius (µm). Left-hand panels for April 2012 and right-hand panels for April 2013. The grey shading refers to the periods when the stem was frozen. The timing of the monoterpene burst is marked with dotted lines in the lower panels.~~

Figure 6. The daily sum of pine stem sap flow in 2012 (red) and 2013 (black). The timings of the monoterpene bursts are marked with dashed lines. The days when the stem was frozen are removed from the figure.

Figure 7. β as a function of time in 2012 and 2013. Figure shows that β (see Eq. 1), i.e. the daily amplitude of the phloem vs. xylem radial change, had its maximum value briefly before and during the monoterpene emission burst (dashed line). Days with occurrences of rain and frozen stem were removed.

Figure 8. Temperature-corrected stem CO_2 efflux anomalies for April 2012 (A) and 2013 (B).