We thank the reviewer #1 for the evaluation of the manuscript and for raising the awareness of the shortcomings in it. The manuscript was revised according to the reviewers' comments. Here the pointby-point answers are given. The reviewers' comments are in bold and our answers are in normal font. The answers are divided into author's response (AR) and author's changes to manuscript (ACM).

The manuscript of the development of a thermal desorption gas chromatography mass spectrometry method for the analysis of monoterpenoids, sesquiterpenoids and diterpenoids is a useful contribution to AMT, but it needs to undergo major revisions before it is published.

#### There are three main issues:

1- The method has already been validated for monoterpenoids and sesquiterpenoids, so all the information in the paper about these compounds is not necessary. Furthermore, there is a strong mix up in the text between monoterpenoids, terepenes and terpenoids which is highly confusing. Since I recommend to use only diterpenoids, this problem will be solved.

AR: These were very useful comments and helped us to improve the manuscript. However, we do not fully agree with the reviewer that the information regarding monoterpenes (MTs) and sesquiterpenes (SQTs) should be excluded from the manuscript. The reasons for this will be explained here and in few points later on. Parts of the reviewers' remarks were maybe caused by the lack of appropriate information we had provided and parts perhaps by the improper terminology we had used occasionally in the original manuscript. These parts have now been revised and improved.

The analytical procedure that we have used in this manuscript has not been validated previously as such for the determination of MTs and SQTs in gas-phase samples. We did apply many parts of the previously developed and optimized in-house analytical procedure for our work. These applied parts of the TD-GC-MS method included, e.g. the thermal desorption units' parameters such as desorption temperature, desorption time, desorption flow rate, cold trap temperature and outlet split flow (although, of course, the desorption efficiency was separately tested in this current work and the desorption time was subsequently increased for TDGCMS2). However, in this work we used different analytical column than previously in gas chromatography (GC), and therefore also different GC oven temperature program. Due to this, also the mass spectrometry (MS) selected ion recording (SIR) time windows were changed from the previously in-house validated TD-GC-MS method. The GC column used previously had the same stationary phase material, but the film thickness was in that 1  $\mu$ m whereas we used here 0.25  $\mu$ m. Less thick stationary phase was selected to elute the DTs in reasonable time and to minimize the column bleed since higher GC temperatures were needed to elute DTs. Nonetheless, many practical aspects of the procedure could be applied from previous works, such as calibration standard preparation, calibration working range, sorbent tube conditioning etc. Therefore, in the original manuscript, we wanted to be transparent that the procedure was partly applied from our groups' previous works, but naturally this was understood in the way that it was the same method and just diterpenes were added as analytes. As explained above, this was not the case. Consequently, this has been made clearer in the revised manuscript. Now the reader does not need to anymore browse to the prior published articles to see the differences in methods, as the main changes have been explained in the revised manuscript.

In our opinion, it is necessary to present the results also for MTs and SQTs for comparability purposes. In many sections of manuscript, the results of DTs are compared specifically to the results of MTs and SQTs. Furthermore, we do not fully agree with the reviewer that the information about MTs and SQTs is not necessary, since even a similar method development manuscript with only MTs and SQTs still would have some novelty. For example, just recently in Atmospheric Measurement Techniques journal an article covering the method development for the online GC-MS analysis of MTs and SQTs was published (Mermet et al., 2020). Thus, there is still novelty for presenting detailed results about the method performance results for MTs and SQTs. In our opinion, one of the strengths of our manuscript is that it presents collectively the results for MTs, SQTs and DTs.

The presentation of terpene classification has been changed (also Reviewer #2 had a comment regarding this). As per Reviewers' later comments, the classification of compounds have been added to the tables and plots in the manuscript. The changes are demonstrated later on here in the answers.

#### ACM: In the Introduction, the following clarification was done:

"In this study, sorbent tube sampling followed by TD-GC-MS analysis for the determination of MTs, SQTs and especially DTs in gas-phase samples was developed and evaluated. The TD-GC-MS method was partially incorporated from our group's previous studies (see e.g. Hellén et al., 2018), and modified accordingly to fit the needs for the analysis of low-volatility diterpenes. In principle, similar analytical procedures have been used previously in both ambient air and enclosure emission studies for the analysis of relatively volatile and semi-volatile MTs and SQTs in multiple field campaigns (Aaltonen et al., 2011;Hellén et al., 2018;Joensuu et al., 2016;Mäki et al., 2017;Vanhatalo et al., 2018). In this work, we build on our previous knowledge of the TD-GC-MS technique and developed our core TD-GC-MS method further to allow the analysis of the fairly low-volatility DTs. In this study, the method development and applicability related experiments done in view for the analysis of DTs included e.g. desorption efficiency, sampling recovery, stability tests, comparison of online and offline sampling modes and ozone reactivity tests. The method analytical figures of merit were also determined, including the quantification limits, intermediate precisions and measurement uncertainties for the terpenes. In addition, qualitative and semi-quantitative experiments were conducted in laboratory and in field conditions to characterise the DTs potentially emitted by boreal forest tree species."

#### In Section 2.2., the following was added as first paragraph:

"As mentioned before in the Introduction, the TD-GC-MS method used here was partially applied from a previously developed and validated in-house method that has been used in our group's previous studies for the analysis of MTs and SQTs (see e.g. Hellén et al., 2012, 2018). In this current work, the stationary phase (nonpolar 1,4-bis(dimethylsiloxy)phenylene analytical GC column polydimethylsiloxane) film thickness was decreased from a previously used thick phase 1.0 μm column to 0.25 µm column as a compromise to maintain proper selectivity between the terpenes and to elute the DTs in reasonable time (chromatograms presented later on). It was expected that the DTs might retain too strongly in the 1.0 µm film thickness column and that the column bleed could become a problem in long-term use since higher temperatures are required to elute the DTs. Thus, the analytical column was replaced, GC oven temperature program was modified, and the MS scan settings were updated and modified. For the most part, the TD unit parameters' were kept as in the previously optimized in-house method, however, the desorption efficiency was separately verified in this work."

# 2- The ambient measurements are not representative. You will never get 60\_C in a boreal environment. Additionally, there is no blank for these measurements, making the experiments quite doubtful. Please discuss why such high increases of temperature are representative for boreal environments, and how likely is for such compounds to really be emitted from this ecosystem.

AR: In general, we do not state that the high temperatures are representative of natural conditions. High temperatures were tested in order: i) to test the developed method in practice in real sample analysis, ii) to identify the DTs potentially emitted by the studied plant material samples and iii) to quantify the emissions of DTs and to compare those in relative terms to MTs and SQTs emissions. In the revised manuscript, we have elaborated the decision to use heating in the experiments more clearly (see ACM). Given that there are no direct results yet about the presence of DTs in boreal environments, we cannot say and do not want to speculate how these compounds are being emitted and if they are being emitted in detectable amounts. It is somewhat out of the scope of our paper. However, we have added information that previous studies have concluded that the DTs are likely emitted from the storage pools of the plants and that the emissions have been seen to be temperature driven (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018). The diterpenes were not solely emitted at 60 °C, e.g. as written in Section 3.2.1 regarding the emissions from pine needles "…and of the five DTs detected in total, only three were above LOQ at 30 °C…". Diterpenes were detected at lower temperatures also, but in less amounts as can be seen in Figs. 8 and 9.

In addition, please note that the developed analytical procedure is not restricted to be used only in boreal environments. As it currently stands in the manuscript, the first line in abstract: "In this study, a thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) method following sorbent tube sampling was developed for the determination of monoterpenes (MTs), sesquiterpenes (SQTs) and diterpenes (DTs) in gas-phase samples."

We thank the reviewer for pointing out that there was no information about blanks. Most importantly, blank measurements were done, but the information was missing from the original manuscript. This will be addressed more carefully later on here in the answers (under Specific comments).

#### ACM: The beginning of Section 2.4 was rewritten and modified:

"Two types of real sample applications were selected in order to test the analytical method performance, to identify compounds emitted by boreal forest tree species and to quantify the emissions from a branch enclosure. The first sample application was a dynamic headspace sampling of compounds emitted by needles/twigs in a closed chamber upon heating, and the second sample application was a study of emissions from a branch enclosure in field conditions. The main emphasis on real sample applications was set on the identification and study of DTs, although MTs and SQTs were also monitored. Based on previous studies, it was considered that since the DTs seem to be emitted from plant storage pools and since temperature has been shown to be a driving force for DTs emissions (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018), heating of the plant materials would be an efficient way for releasing the DTs into gas-phase. Thus, the studied plant material samples were firstly heated to temperatures ranging from 30 °C to up to 70 °C in order to obtain presumably detectable amounts of DTs to allow their identification and quantification."

#### In the Section 3.2 the following was added:

"As explained in Section 2.4., in the following experiments the plant material samples were heated in order to characterize the DTs potentially emitted by the studied tree species and to further test the TD-GC-MS method performance in view of real sample analysis. The plant material samples were heated to facilitate the release of DTs from the plant storage pools into the gas-phase."

# 3- Method development. The paper needs definitions on method development and validation. Please explain how this is different from previous studies. Furthermore, please discuss while you develop a method for quantification but at the end, for real samples you use a different system and you only give semi-quantitative information.

AR: The term validation was removed from the manuscript and it was replaced with a more appropriate term analytical figures of merit. This was considered to being more representative for the purpose of this manuscript, although much of the work we conducted falls within the context of method validation. Most of the tests and experiments performed were done for testing and demonstrating that the developed analytical procedure is suitable for its intended purpose, i.e. that the developed method can be used for the analysis of MTs, SQT and most importantly DTs.

In the revised version it has been made clearer how this is different from previous studies (see AR and ACM above to point 1).

The TD-GC-MS2 was used for the other real sample analysis since the TD-GC-MS1 was not available for analysis at the time of these experiments. The TD-GC-MS2 chromatograms from standard and sample analyses are presented in Figs. S8 and S20, respectively. The TD-GC-MS2 was well suited for the analysis of the analytes. The main differences between the TD-GC-MS units are presented in Table S2 and in Section 2.2 (i.e. differences were the models of units, different cold traps and GC columns installed (column stationary phases were the same, but the total length of columns were different and column manufacturers were different). In the revised manuscript, a mentioning about the TD-GC-MS1 not being simply available for analysis was added and a note about column length.

The results are semi-quantitative since the non-target compounds detected in real sample analysis were quantified based on the standard analyte compounds. This is explained in Section 2.5 second paragraph. This paragraph was rephrased and modified in the revised manuscript.

ACM: Please see the ACM above in point 1 to see the changes covering the difference to previous studies. In addition to those, the following changes were made:

Validation was removed and replaced accordingly in all parts of the manuscript.

In the abstract: "The analytical figures of merit were determined, and the method performance was tested by conducting experiments related to, for example, sampling recovery, storage stability and ozone reactivity."

In Section 2.2.: "Most of the analytical method development and performance tests were conducted with TD-GC-MS1"

In Section 2.3.5 title was changed to "2.3.5 Analytical figures of merit"

In Section 3.1.4 title was changed to "3.1.4 Analytical figures of merit of the developed TD-GC-MS method" and in this section the following changes were made "The analytical figures of merit are shown in Table 1."

Regarding semi-quantitative results, in Section 2.5, the second paragraph was modified:

"The non-target compounds detected in real samples were quantified by using a compound from the standard analytes list ( $\alpha$ -pinene, limonene or linalool were used for MTs and for close eluting BVOCs,  $\beta$ -caryophyllene or caryophyllene oxide for SQTs and for close eluting BVOCs, and cembrene or ent-kaurene were used for DTs and close eluting BVOCs). Since the non-target compounds were quantified in this manner, the mass concentration results are merely semi-quantitative. A signal-to-noise (S/N) ratio of 10 criteria was used in non-target compound quantification. Similar quantification procedure for non-target compounds has been used also in previous BVOC studies (e.g. Bouvier-Brown et al., 2009; Haberstroh et al., 2018; Hellén et al., 2018)."

Regarding the use of TD-GC-MS2 for analysis of real sample, a comment was added to Section 3.2.2 first paragraph ending: "TD-GC-MS2 was used for analysis since the TD-GC-MS1 was not available at the time of these experiments."

The differences between the units to Section 2.2.: "...The main differences in these TD-GC-MSs were the models of units, different cold traps and columns (same stationary phases, but 10 m shorter column in TD-GC-MS2) installed..."

#### Specific comments:

Page 1 Line 14: Despite I think ozone reactivity of diterpenes is important and should be stated in the paper, it is really not introduced in the text. . . how these measurements add to your method validations. It must be better introduced here in abstract and in text.

AR: Ozone is one very important factor causing losses of the studied compounds during the sampling. Therefore it is very important to know how reactive these compounds are and how fast they are lost by the ozone. Some ozone removal methods can be used, but most of them are also prone to cause losses or isomerization of the terpenes. Therefore it is very important to know how long we can sample without using any ozone removal methods, if needed.

ACM: Sentences "Ozone is an important factor causing losses of the studied compounds during sampling. Therefore, losses of terpenes upon ozone exposure were studied and the reaction rate coefficients were estimated" added to the abstract.

And sentence "It is well-known that compounds can be lost during sampling due to reactions with ozone" was added to Section 2.3.6 Ozone reactivity tests.

## Page 1 line 19: I do not understand why heating up to 60\_C is representative of anything natural, you will never get these temperatures in boreal ecosystems. In which way these diterpenes will then be emitted to ambient air?

AR: We did not try to represent specifically real emissions. We simply ended up testing fairly high temperatures in order to characterize the DTs possibly emitted by the studied boreal forest tree species and to test the developed analytical procedure in practice. It was thought to be likely that the diterpenes emitted in the laboratory experiments and proof-of-concept experiments would be the same diterpenes emitted in natural conditions.

It is out of the scope of this study to speculate how the DTs would be emitted in real conditions. Longterm measurement campaigns are needed to study the emissions and only then we can investigate under which real-life conditions the DTs are emitted (if they are emitted at all in detectable levels in boreal forest). This is also stated in the Conclusions. The diterpenes were also emitted at lower temperatures (as can be seen in the Figs. 8 and 9), although in much lower amounts. Nonetheless, we have explained our decision to use high temperatures more clearly in the revised manuscript (essentially the same modification as in major comment point 2).

The decision to test also high temperatures are given in the manuscript later on.

#### ACM: In Section 2.4:

"Two types of real sample applications were selected in order to test the analytical method performance, to identify compounds emitted by boreal forest tree species and to quantify the emissions from a branch enclosure. The first sample application was a dynamic headspace sampling of compounds emitted by needles/twigs in a closed chamber upon heating, and the second sample application was a study of emissions from a branch enclosure in field conditions. The main emphasis on real sample applications was set on the identification and study of DTs, although MTs and SQTs were also monitored. Based on previous studies, it was considered that since the DTs seem to be emitted from plant storage pools and since temperature has been shown to be a driving force for DTs emissions (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018), heating of the plant materials would be an efficient way for releasing the DTs into gas-phase. Thus, the studied plant material samples were firstly heated to temperatures ranging from 30 °C to up to 70 °C in order to obtain presumably detectable amounts of DTs to allow their identification and quantification."

In the Section 3.2 the following was added:

"As explained in Section 2.4., in the following experiments the plant material samples were heated in order to characterize the DTs potentially emitted by the studied tree species and to further test the TD-GC-MS method performance in view of real sample analysis. The plant material samples were heated to facilitate the release of DTs from the plant storage pools into the gas-phase."

#### Page 1 Line 20: five what?

AR: Five DTs in the pine needle emissions. For clarification word 'DTs' was added after the five.

ACM: "..., five DTs and 13 DTs could be..."

#### Page 1 Line 20: it is really not acceptable that you provide a method validation to then deliver semiquantitatively.

AR: We did not have standards for the non-target compounds, hence the emission rate results were presented as semi-quantitative. This is a common practice in non-target analysis, where it is common that the analyst does not possess all the pure compounds for calibration (and quantification). This process is explained in the revised manuscript Section 2.5 in the second paragraph. No changes were made to the Abstract regarding this.

Page 2 Line 41. The way you express monoterpenoids (as well as sesquiterpenoids and diterpenois) is really confusing. By omitting mt and sqt this problem will be solved. But please do explain what do you mean by monoterpene and monoterpenoid. . . for instance, is p-cymene not a monoterpenoid? And it is only C10H14...In fact, you could name them in Table 1, S4,S5.

AR: The classification and terminology was updated and these were added in Tables as suggested by the reviewer. This change was also done based on the Reviewer #2 comments. Now it should be hopefully clear to which compounds we refer to since these are classified and shown in all the Tables. The text was revised throughout the manuscript/supplement accordingly. In addition, the title was changed to "...monoterpenes, sesquiterpenes and diterpenes".

ACM: The terminology has been changed throughout the manuscript. As an example, the compound categories were added Section 2.1. and Table 1: "The analyte included nine MTs (both hydrocarbon and oxygenated MTs), six SQTs (both hydrocarbon and oxygenated SQTs), three diterpenes (all hydrocarbon DTs) and three other compounds that were categorised here as BVOCs." Revised Table 1:

Table 1. List of analy	tes, correspond	ing retention	i maices (i	KI) and a	narytical figu	Deres of mer	11.		
Compound	CAS Number	Formula	RIª	Quan -tify m/z ion	LOQ in pg (in pptv) <sup>b</sup>	repea tabilit y (RSD %)	Inter- mediate precision (RSD%)	U <sup>c</sup> (%)	U <sup>d</sup> (%)
α-Pinene (MT)	7785-70-8	$C_{10}H_{16}$	945 (942)	93	34 (1.2)	2.6	3.8	16	18
camphene (MT)	79-92-5	$C_{10}H_{16}$	963 (960)	93	14 (0.5)	1.6	4.0	16	18
β-pinene (MT)	19902-08-0	$C_{10}H_{16}$	989 (988)	93	13 (0.5)	4.2	3.2	17	20
3-carene (MT)	498-15-7	$C_{10}H_{16}$	1018 (1017)	93	18 (0.6)	2.0	3.3	16	17
<i>p</i> -cymene (MT)	99-87-6	$C_{10}H_{14}$	1033 (1031)	119	20 (0.7)	2.0	4.2	17	19
limonene (MT)	5989-54-8	$C_{10}H_{16}$	1039 (1037)	68	62 (2.2)	1.5	3.8	17	17
1,8-cineol (MT)	470-82-6	$C_{10}H_{18}O$	1044 (1042)	154	27 (0.9)	2.6	4.7	18	20
terpinolene (MT)	586-62-9	$C_{10}H_{16}$	1094 (1093)	121	65 (2.3)	2.5	5.0	17	18
linalool (MT)	78-70-6	$C_{10}H_{18}O$	1100 (1100)	71	88 (2.8)	2.4	4.8	18	18
4-acetyl-1- methylcyclohexene (4-AMCH) (BVOC)	6090-09-1	$C_9H_{14}O$	1140 (1139)	95	120 (4.2)	2.7	6.3	19	20
nopinone (BVOC)	38651-65-9	C <sub>9</sub> H <sub>14</sub> O	1154 (1153)	83	29 (1.0)	2.7	5.3	18	21
bornylacetate (BVOC)	5655-61-8	C <sub>12</sub> H <sub>20</sub> O 2	1295 (1294)	95	49 (1.2)	2.4	6.2	20	23
longicyclene (SQT)	1137-12-8	$C_{15}H_{24}$	1401 (1401)	94	35 (0.8)	2.4	4.9	18	21
isolongifolene (SQT)	1135-66-6	$C_{15}H_{24}$	1422 (1422)	161	38 (0.9)	2.5	5.7	19	22
β-caryophyllene (SQT)	87-44-5	$C_{15}H_{24}$	1445 (1444)	93	105 (2.5)	2.2	3.5	17	22
β-farnesene (SQT)	18794-84-8	$C_{15}H_{24}$	1457 (1456)	69	198 (4.7)	5.0	5.9	20	22
α-humulene (SQT)	6753-98-6	$C_{15}H_{24}$	1481 (1480)	93	33 (0.8)	2.1	4.2	18	24
caryophyllene oxide (SQT)	1139-30-6	$C_{15}H_{24}O$	1612 (1612)	79	340 (7.5)	18.9	8.6	24	28
cembrene (DT)	1898-13-1	$C_{20}H_{32}$	1959 (1959)	93	287 (5.1)	4.0	9.5	27	52
ent-kaurene (DT)	562-28-7	$C_{20}H_{32}$	2106 (2106)	257	518 (9.3)	2.9	7.7	26	42
3-methylene-5-α- androstane (3-MA) <sup>e</sup> (DT)	not assigned	$C_{20}H_{32}$	2153 (2152)	257	383 (6.9)	3.0	7.2	-	-

Table 1. List of analytes, corresponding retention indices (RI) and analytical figures of merit.

<sup>a</sup> RI as Kovats indices (and arithmetic indices in brackets)

 $^b$  LOQ in pptv calculated by using sample volume of 5 L (at T=298 K and p=1 atm)  $^c$  U (%) for ambient air application

<sup>d</sup> U (%) for branch enclosure application

<sup>e</sup> The purity of this crude standard was set to being 100% (allowing the determination of LOQ, but unknown uncertainty).

### Page 2 line 62. This is confusing, please state which branch enclosure you are referring and which ambient studies? Do you mean you experiments or the previously reported studies?

AR: This paragraph of the Introduction section was largely modified. To this particular part, the references were added, and the sentences were rephrased.

ACM: "...In general, previously offline (and online) TD-GC-MS technique has been mainly used for the analysis of MTs and SQTs (Hellén et al., 2018;Mermet et al., 2019; Pankow et al., 2012), but the abovementioned branch enclosure and ambient air studies indicate that this analytical technique is also applicable for the analysis of DTs (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018). Unfortunately, most of those studies did not present any detailed method descriptive performance parameters for DTs (e.g. detection limits, reproducibility, selectivity or sampling recovery), making it difficult to critically evaluate the suitability of the analytical procedures for the analysis of low volatility DTs (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018)..."

Page 2 Line 63. If you are going to say this, you need to explain what do you mean by method validation. Do you need two different analytical systems to prove your concentrations? And what do you mean by performance parameters? GC and sampling settings? In is normally well mentioned in the methods of each study? Please state why you method is 1) better than previously mentioned for DT measurements, and 2) how you truly validate the method rather than say your method is good because I do not loose DT in the lines...

AR: This paragraph of the Introduction section was modified.

In those referred DT publications, two out of six publications gave only limit of detection values for DTs, the other four either do not mention detection limits or if they do, those are only for MTs and SQTs. Information about, for example, calibration range, repeatability, reproducibility, selectivity, uncertainty or recovery concerning DTs is not directly presented in most of the DT studies. This is what we tried to discreetly say in the Introduction section. In principle, analytical procedures used for MTs and SQTs (and other BVOCs or VOCs) have been applied to analyze DTs, but there is no separate information presented that shows that the methods are reliable for that purpose. Of course, it could be argued that the ambient results indicate that the methods have worked, but strictly speaking, since there are no experimental tests showing clearly the performance parameters, there is a justified reason for questioning the applicability of such analytical procedures for DT analysis. In many of those studies, there have been statements that the concentrations of DTs might be underestimated due to sampling line losses, however, the recoveries of DTs have not been separately tested.

To the point 1): In the manuscript, we do not declare that our method is better than the previously used methods for the analysis of DTs in gas-phase samples. Actually, it is quite difficult to compare our method to the ones already existing, since as explained above, those methods unfortunately do not have that much information about DTs presented to compare to. In the manuscript Section 3.1.4, we compare our LOQ values to the detection limits presented in one prior publication (the one publication that showed detection limits in comparable units for DTs). However, no changes regarding this were made to the Introduction section.

To the point 2): The term validation was removed from the manuscript and it was replaced with a more appropriate term analytical figures of merit. This was considered to being more representative for the purpose of the manuscript, although much of the work we conducted falls within the context of method validation. We hope this terminological change satisfies the reviewers' concerns related to

method validation. In general, the experiments performed to demonstrate that the method is suitable for its intended purpose included, for example: selectivity and specificity (showed chromatographic separation, compounds identified with mass spectrometry), repeatability (done six repetitions of a standard sample during one day), intermediate precision (done 22 repetitions of a standard sample during 4.5 months period), limit-of-quantification (determined by analyzing 10 blanks), calibration ranges, recoveries (different inlet sampling lines tested), compound stability during storage (tested different storage times), estimation of measurement uncertainty and finally the real sample application tests.

#### ACM:

In the Introduction section, one paragraph was largely rewritten:

"Diterpenes have fairly low vapor pressures and they can be categorised as semi-or low-volatile organic compounds. The determination of DTs in atmospheric gas-phase samples can be challenging due to their low-volatility and high reactivity, which might cause sampling line losses and emphasize the need for high-sensitivity detection methods (Yáñez-Serrano et al., 2018;Yee et al., 2018). In previous atmospheric studies, DTs have been analysed by using either conventional chromatographic techniques or online mass spectrometric techniques (such as proton-transfer-reaction mass spectrometry) (Chan et al., 2016; Haberstroh et al., 2018; Li et al., 2019; Matsunaga et al., 2012; Yáñez-Serrano et al., 2018; Yee et al., 2018). Many of those chromatographic studies targeting DTs used traditional sorbent tubes for sampling prior to thermal desorption (or solvent desorption)-gas chromatography-mass spectrometry (TD-GC-MS) analysis (Haberstroh et al., 2018; Matsunaga et al., 2012; Yáñez-Serrano et al., 2018). In general, previously offline (and online) TD-GC-MS technique has been mainly used for the analysis of MTs and SQTs (Hellén et al., 2018;Mermet et al., 2019; Pankow et al., 2012), but the above-mentioned branch enclosure and ambient air studies indicate that this analytical technique is also applicable for the analysis of DTs (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018). Unfortunately, most of those studies did not present any detailed method descriptive performance parameters for DTs (e.g. detection limits, reproducibility, selectivity or sampling recovery), making it difficult to critically evaluate the suitability of the analytical procedures for the analysis of low volatility DTs (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018). In general, sorbent tube sampling followed by TD-GC-MS analysis methods have been demonstrated to be suitable for the analysis of MTs, however, there is very little detailed information about the suitability for the analysis of SQTs (Bouvier-Brown et al., 2009;Helmig et al., 2004; Jones et al., 2014; Mermet et al., 2019; Pankow et al., 2012), and data related to DTs is currently lacking"

In the Introduction section last paragraph, the following clarification was done: "In this work, we build on our previous knowledge of the TD-GC-MS technique and developed our core TD-GC-MS method further to allow the analysis of the fairly low-volatility DTs. In this study, the method development and applicability related experiments done in view for the analysis of DTs included e.g. desorption efficiency, sampling recovery, stability tests, comparison of online and offline sampling modes and ozone reactivity tests. The method analytical figures of merit were also determined, including the quantification limits, intermediate precisions and measurement uncertainties for the terpenes. In addition, qualitative and semi-quantitative experiments were conducted in laboratory and in field conditions to characterise the DTs potentially emitted by boreal forest tree species."

Validation was removed and replaced accordingly in all parts of the manuscript as follows: In the abstract: "The analytical figures of merit were determined, and the method performance was tested by conducting experiments related to, for example, sampling recovery, storage stability and ozone reactivity." In Section 2.2.: "Most of the analytical method development and performance tests were conducted with TD-GC-MS1"

In Section 2.3.5 title was changed to "2.3.5 Analytical figures of merit"

In Section 3.1.4 title was changed to "3.1.4 Analytical figures of merit of the developed TD-GC-MS method" and in this section the following changes were made "The analytical figures of merit are shown in Table 1."

Page 3 Line 69-78. In your objectives are somehow confusing. First you talk about the applicability of sorbent tubes and GCMS for mt, sqt and dt. I do not know what is new here. This has been shown in the past, plus this is no objective, but rather telling what you did. Later you say the method was incorporated from previous studies for sqt and mt. Thus there is no novelty on sqt and mt, so this builds my point of removing mts and sqt from the text. Then you say you do a method development for dt, and it is not clear to me what is the actual development (not just simply that you have calculated the LOD. . ... But rather than the lod is lower than using this other method. . ...) as compared to mt and sqt analysis. It is also very strange to me that you offer a validated method and then you report only semi-quantitative values. Thus the whole objectives section must be rewritten. Please bear in mind to put what do you intent to do and why.

AR: Please see the AR's and ACM's to main comments 1-3. This objectives paragraph was rewritten partly as suggested. Some of the results were semi-quantitative since we did not have pure standards for the non-target compounds.

ACM: The last paragraph of Introduction was largely rephrased and rewritten:

"In this study, sorbent tube sampling followed by TD-GC-MS analysis for the determination of MTs, SQTs and especially DTs in gas-phase samples was developed and evaluated. The TD-GC-MS method was partially incorporated from our group's previous studies (see e.g. Hellén et al., 2018), and modified accordingly to fit the needs for the analysis of low volatility diterpenes. In principle, similar analytical procedures have been used previously in both ambient air and enclosure emission studies for the analysis of relatively volatile and semi-volatile MTs and SQTs in multiple field campaigns (Aaltonen et al., 2011;Hellén et al., 2018;Joensuu et al., 2016;Mäki et al., 2017;Vanhatalo et al., 2018). In this work, we build on our previous knowledge of the TD-GC-MS technique and developed our core TD-GC-MS method further to allow the analysis of the fairly low-volatility DTs. In this study, the method development and applicability related experiments done in view for the analysis of DTs included e.g. desorption efficiency, sampling recovery, stability tests, comparison of online and offline sampling modes and ozone reactivity tests. The method analytical figures of merit were also determined, including the quantification limits, intermediate precisions and measurement uncertainties for the terpenes. In addition, qualitative and semi-quantitative experiments were conducted in laboratory and in field conditions to characterise the DTs potentially emitted by boreal forest tree species."

#### Page 3 Line 83: If one of the dt standard is not analytically valid, then you have to skip it.

AR: It was written "not analytically valid in terms of purity and traceability". By purity, it was meant that the supplier did not provide purity of the compound, it was merely a crude standard. By traceability, it was meant that no CAS number is assigned to the compound. However, the compound was purchased from a major supplier (Sigma-Aldrich, Table S1) and should be available for others if they are interested in reproducing our analytical procedure. We merely wanted to be transparent in the manuscript so that reader is aware of this limitation of the chemical. In our opinion, there is no apparent reason for removing the results of this compound.

#### Page 3 Line 84-86. Delete sentence

AR: In this sentence, we elaborate the reason for why we had only three DTs as standards and also emphasize the reason for including MTs and DTs as analytes. We prefer to keep this sentence in the manuscript, however, the sentence was modified a bit to make the reasoning clearer.

ACM: "The current supply situation of DTs is not optimal for the purpose of comprehensive method development, however, together with the results of MTs and SQTs to compare to, valuable information was expected be obtained even with only few DTs included as analytes."

### Page 3 Line 88: Please state why do you dilute the standards in methanol and not other solvent such as hexane.

AR: Most importantly, all the analytes are soluble in methanol. Also, methanol is a good solvent in practice for the calibration setup, since it volatilizes easily in the nitrogen stream. Other less volatile solvents might retain in the sorbent and be observable in relatively large amounts in the chromatograms. This was added in Section 2.1 together with a reference to previous work.

ACM: In Section 2.1 last paragraph: "Calibration tubes were prepared by injecting 5  $\mu$ L of individual standard solution into the tube and simultaneously applying 80 mL min<sup>-1</sup> flow of nitrogen ( $\geq$ 99.9999 % AGA, Espoo, Finland). The tubes were purged for 10 min in order to evaporate the excess methanol (Hakola et al., 2003)."

Page 3 line 88 and 90. You can't report such a large range in concentrations for analyte solutions. You must be certain of the concentration of your solution, and this is why you use calibrated pipettes. So please change accordingly. If you have a range of concentrations due to different compounds, then state them in a table.

AR: Indeed we do have different concentrations for different compounds. Individual analytes were weighted in the same flask, thus the analytes were mixed in the same standard solutions. The ranges are expressed for different compound categories later on in the manuscript (see the answer to second following comment from this comment), however, we also rephrased slightly this Section 2.1 second paragraph. It was added that the solutions were a mixture of compounds and that the range expressed depended on the compound.

ACM: In section 2.1: "Primary standard mix solutions of the target compounds were prepared by weighting and diluting the pure compounds in methanol. The analyte concentrations in primary solution were in the range of  $40-200 \text{ mg L}^{-1}$  depending on the compound."

#### Page 3 line 91. Why do you store solutions in the dark at 4\_C?

AR: Some of the pure analytes are recommended to be stored at 2-8 °C (e.g.  $\alpha$ -pinene,  $\alpha$ -humulene and ent-kaurene), thus also the standards were stored at 4 °C. They were mostly "in the dark", since the refrigerator light turns off when the door is closed. No changes were made to the manuscript.

### Page 4 line 103-104. I do not understand this sentence. Please rephrase thinking what is the point of this statement to the objective of the paper.

AR: The point is to show the calibration standard concentration ranges. The sentence was rephrased by adding "...calibration concentration ranges..." and by decreasing the number of decimals shown and putting the "expressed as absolute amount (ng) in sorbent tube" at the end in parenthesis.

ACM: "The calibration concentration ranges were 0.2–55.8 ng for MTs, 0.2–61.2 ng for SQTs, 0.4–200 ng for DTs and 0.2–43.2 ng for other BVOCs (expressed as absolute amount (ng) in sorbent tube)."

#### Page 5 Line 130: why you changed the method (different final state) for TDGCMS2?

AR: The column (different manufacturer, but same stationary phase) in TDGCMS2 was 10 m shorter than the column in TDGCMS1 (Table S1). Also, it was considered that it is beneficial for the column lifetime to shorten the final state hold temperature. It did not change the separation of the compounds. A separate mention about the column length was added to earlier part in Section 2.2.

ACM: "...different cold traps and columns (same stationary phases, but 10 m shorter column in TD-GC-MS2) installed."

#### Page 5 Line 136-140: I think this information is useless, either rephrase or remove.

AR: These lines were removed from this Section 2.3, however, parts of the original information was modified and added to the beginning of Section 2.2.

ACM: "As mentioned before in the Introduction, the TD-GC-MS method used here was partially applied from a previously developed and validated in-house method that has been used in our group's previous studies for the analysis of MTs and SQTs (see e.g. Hellén et al., 2012, 2018). In this current work, the analytical GC column stationary phase (nonpolar 1,4-bis(dimethylsiloxy)phenylene polydimethylsiloxane) film thickness was decreased from a previously used thick phase 1.0  $\mu$ m column to 0.25  $\mu$ m column as a compromise to maintain proper selectivity between the terpenes and to elute the DTs in reasonable time (chromatograms presented later on). It was expected that the DTs might retain too strongly in the 1.0  $\mu$ m film thickness column and that the column bleed could become a problem in long-term use since high temperatures are required to elute the DTs. Thus, the analytical column was replaced, GC oven temperature program was modified, and the MS scan settings were updated and modified. For the most part, the TD unit parameters' were kept as in the previously optimized in-house method, however, the desorption efficiency was separately tested and verified in this work."

#### Page 5 Line 146: please state how many tubes were stored.

AR: Done.

ACM: "...was evaluated by storing the tubes (n=2-6) sealed..."

### Page 6 line 186: please state which are the guidelines so the reader doesn't need to go somewhere else to find it. You can do it in SI if you don't want this info in the text.

AR: This was done as the reviewer suggested by showing the formulas in Supplementary material. We also improved the presentation of the measurement uncertainties by showing the U values for two applications in which the developed analytical procedure could be used: i) offline sorbent tube sampling of ambient air followed by TD-GC-MS analysis and ii) offline sorbent tube sampling of emissions from a branch enclosure cuvette followed by TD-GC-MS analysis.

ACM: The sentence was changed: "The expanded measurement uncertainty (U) was estimated from partial uncertainties by following ACTRIS (Aerosol Clouds Trace gases Research InfraStructure) guidelines (ACTRIS, 2018). The U (%) was estimated for two analytical procedures: i) offline sorbent tube sampling of ambient air followed by TD-GC-MS analysis and ii) offline sorbent tube sampling of

emissions from a branch enclosure cuvette followed by TD-GC-MS analysis. The intermediate precision and recovery experiment results were included in the calculations of U. In the ambient air sampling procedure, the ozone removal inlet recovery results were used in the calculations, whereas in the branch enclosure emissions procedure the cuvette recovery results were used in the calculations. A more detailed description of the uncertainty calculations can be found in Supplement Text S1."

In supplement the following has been added:

#### "TEXT S1. Expanded measurement uncertainty

The expanded measurement uncertainty (U) was estimated from partial uncertainties of the procedures by following ACTRIS (Aerosol Clouds Trace gases Research InfraStructure) guidelines (ACTRIS, 2018). The U was estimated separately for two analytical procedures: i) offline sorbent tube sampling of ambient air followed by TD-GC-MS analysis and ii) offline sorbent tube sampling of emissions from a branch enclosure cuvette followed by TD-GC-MS analysis.

The combined standard uncertainty (total uncertainty,  $uX_{total}$ ) includes both the random and systematic errors affecting the measurements. In this work, the  $uX_{total}$  was calculated for both procedures i) and ii) by using Eq. (S1):

$$u\mathcal{X}_{\text{total}}^{2} = u\mathcal{X}_{\text{prec}}^{2} + u\mathcal{X}_{\text{stdprep}}^{2} + u\mathcal{X}_{\text{vol}}^{2} + u\mathcal{X}_{\text{rec}}^{2} , \qquad (S1)$$

where  $u \mathcal{X}_{prec}$  is the precision component taking into account random errors,  $u \mathcal{X}_{stdprep}$  is the uncertainty due to calibration standard preparation,  $u \mathcal{X}_{vol}$  is the component descriptive of systematic errors in the sample volume determination and  $u \mathcal{X}_{rec}$  is the recovery component taking into account the losses in sampling lines and/or cuvette.

The  $u \chi_{\text{prec}}$  was calculated by following Eq. (S2):

$$u\mathcal{X}_{\text{prec}}^{2} = \left(\mathcal{X}_{\text{sample}} * \sigma_{\text{series}}^{rel}\right)^{2} + \left(\frac{x_{\text{LOD}}}{3}\right)^{2}, \qquad (S2)$$

where  $\mathcal{X}_{sample}$  is the concentration of the analyte,  $\sigma_{series}^{rel}$  is the intermediate precision expressed as relative standard deviation and  $x_{LOD}$  is the limit of detection (LOD) value. The intermediate precision was obtained from analysing standard samples (*n*=22) during 4.5 months period (Section 2.3.5). The  $x_{LOD}$  was determined by analysing multiple blank sorbent tubes (*n*=10), and then by calculating the standard deviation of peak area in blanks and by multiplying the standard deviation by three.

The  $uX_{stdprep}$ , was derived by taking into account the uncertainties originating from weighting (mass balance error), pipetting (volumetric pipette error) and diluting (volumetric flask error) the standard compounds. The  $uX_{stdprep}$  was eventually calculated by setting a 5% uncertainty, as in Hellen et al. (2002), for all the analytes included in this work. This was considered as an upper estimate for the calibration standard preparation uncertainty.

The  $uX_{vol}$  was estimated based on the uncertainty of the offline sampling by estimating the collective uncertainty related to sampling flow rate and sampling time. In this work, the  $uX_{vol}$  for all compounds was derived by using a set 5% uncertainty. This was considered as being an upper estimate for the sampling volume uncertainty.

The  $u \chi_{rec}^2$  was calculated based on the sampling line recovery results by using Eq. (S3):

$$u\mathcal{X}_{\text{rec}}^{2} = \left(\mathcal{X}_{\text{sample}} * \sqrt{\frac{\Sigma(bias)^{2}}{n}}\right)^{2},$$
(S3)

where  $\mathcal{X}_{sample}$  is the concentration of the analyte, *bias* is the deviation of the observed relative recovery from the 100% recovery and *n* is the number of different measurements. The recovery results obtained with the 1 m long ozone removal inlet at two different relative humidity (RH) levels (RH=0% and RH=100%) were used for the procedure i), whereas the recovery results obtained in the cuvette experiments at flow rates 2.0 L/min and 6.7 L/min were used for the procedure ii) (see Sections 2.3.3 and 3.1.3). These were considered to being representative of real applications. In procedure i), ambient air can be sampled directly via short ozone removal inlet (as in e.g. Hellen et al., 2018). In procedure ii), the sorbent tubes are sampled from the cuvette outlet port, therefore, there is no need for long sampling lines and ozone removal inlet is not needed since the incoming air is zero VOC free air (as in e.g. Hakola et al., 2006).

Finally, the expanded measurement uncertainty (U) was calculated by using Eq. (S4):

$$U = 2 * u \mathcal{X}_{\text{total}} = 2 * \left(\frac{u \mathcal{X}_{\text{total}}}{\mathcal{X}_{\text{sample}}} * 100\%\right).$$
(S4)

A coverage factor of k=2 was used for providing a level of confidence of 95 % and the uncertainty was finally converted to relative amount to expresses the U in percentage. The expanded measurement uncertainties for both procedures are presented in the main text Table 1.

#### References

ACTRIS, 2018. Deliverable 3.17. Updated Measurement Guideline for NOx and VOCs, available at: https://www.actris.eu/Portals/46/Documentation/actris2/Deliverables/public/WP3\_D3.17\_M42.pdf?ve r=2018-11-12-143115-077. (last access:27 March 2020).

Hellén, H., Hakola, H., Laurila, T., Hiltunen, V., and Koskentalo, T.: Aromatic hydrocarbon and methyl tert-butyl ether measurements in ambient air of Helsinki (Finland) using diffusive samplers, Sci. Tot. Environ., 298, 55-64, 2002.

Hellén, H., Praplan, A. P., Tykkä, T., Ylivinkka, I., Vakkari, V., Bäck, J., Petäjä, T., Kulmala, M., and Hakola, H.: Long-term measurements of volatile organic compounds highlight the importance of sesquiterpenes for the atmospheric chemistry of a boreal forest, Atmos. Chem. Phys., 18, 13839-13863, doi:10.5194/acp-18-13839-2018, 2018.

Hakola, H., Tarvainen, V., Bäck, J., Ranta, H., Bonn, B., Rinne, J., and Kulmala, M.: Seasonal variation of mono- and sesquiterpene emission rates of Scots pine, Biogeosciences, 3, 93-101, doi:10.5194/bg-3-93-2006, 2006. "

### Page 7 line 206: at what temperature did you store it? Then you freeze the material? is not clear how you did it.

AR: There was a wrong word in this sentence that made no sense for the reader. It should have been written *freezer* instead of *refrigerator*. In order to avoid any further confusion, the wording was replaced with temperature.

ACM: "The samples were stored in the dark at -18 °C for a maximum of 2 months prior to analysis."

### Page 7 line 214: what do you mean as a proof-of-concept type of experiment? And please state if the branch enclosure was just a branch or it also had needles in.

AR: The branch had needles. This information was added.

Proof-of-concept type of experiment refers here to a design of a experiment that demonstrates that the developed method works in a practical application, i.e. that the analytical procedure is suitable for the purpose it was developed. This was added to the revised version of the manuscript.

#### ACM: The following corrections were done:

"Spruce (Picea abies) branch with needles was placed inside..."

"Branch enclosure emissions were studied on-site at the SMEAR II station as a proof-of-concept type of experiment on two different days (i.e. to test and to demonstrate that the analytical procedure is suitable for the purpose it was intended for)."

#### Page 7 line 215: What do you mean but shrank?

AR: It was meant that it was the same cuvette (Teflon bag) as in Section 2.3.3, but that the volume of the bag was made smaller (from 6.2 L to 1.2 L). This part of the sentence in parenthesis was removed since the information was not really necessary.

ACM: "Spruce (Picea abies) branch with needles was placed inside a ca. 1.2 L Teflon bag cuvette, which was connected to a fixed plate with inlet and outlet ports."

#### Page 7 line 217: state reason for copper tube.

AR: Copper tube was used for improving the heat transfer, if that is what the referee is meaning with this. Any other metal tubing could have worked, but copper was easily available to us. This was made clearer.

ACM: "...and passed through a ca. 1 m long copper tube (o.d. 12 mm) wrapped with a heating wire and insulator cover (copper tubing was used for improving heat transfer). The incoming air was heated to increase the cuvette inside temperature...."

### Page 7 line 219: what is the reason of artificially promote BVOC emissions? Why would you do this if it is not realistic to the ecosystem of interest.

AR: Maybe the wording *artificially* is a bit awkward in this context, but as it was said earlier in the paragraph, this was a proof-of-concept type of experiment. The point was to test the method in practice with a similar type of setup that would be employed in a conventional monitoring campaign. The decision to use heating came after the laboratory experiments (i.e. after the results presented in Section 3.2.1). However, this part of the sentence was rephrased by removing "artificially" and by replacing BVOCs with DTs, since the decision to use heating was related specifically to DTs.

ACM: "The incoming air was heated to increase the cuvette inside temperature in order to promote the emissions of DTs."

### Page 7 application to real samples. I do not see any blank measurements, please include them. If you have not taken blank measurements then I ask how do you exclude contamination effects.

AR: Thank you for pointing this out. Blanks were done always before the real samples were collected, but in the original manuscript this information was missing. The blank levels were so low (target/non-target compounds were absent in them) that there was no need for blank subtraction. In the real sample applications, blank samples were used to check possible contaminant peaks from real sample peaks. It was a mistake not to include this information in the original manuscript (it was simply forgotten since no blank subtraction was needed but blanks' information should have been included

since blanks were used to check that the peaks were speciated correctly). This information has been now added to the manuscript.

ACM: Information was added to Section 2.4:

"Blank samples (empty chamber heated) were collected prior to experiments." "Blank samples (empty cuvette heated) were collected prior to experiment."

Information was added to Section 2.5:

"The analysed blank samples were used to exclude possible contaminant peaks."

"No blank subtraction was needed in the calculations since most analytes were absent in the blank samples."

Blank chromatograms were added to Figs. 6 and 7 (old supplementary Figs. S19 and S20):



"Figure 6. Selected ion recording (SIR) chromatograms from the TD-GC-MS1 analysis of pine needles and blank dynamic headspace sorbent tube samples (sampling at 60 °C for 20 min at a flow rate of 100 mL/min)..."



"Figure 7. Selected ion recording (SIR) chromatograms from the TD-GC-MS1 analysis of spruce twigs and blank dynamic headspace sorbent tube samples (sampling at 60 °C for 20 min at flow rate of 100 mL/min)..."

#### Page 8 line 231: what is the sufficient confidence?

AR: As stated in the sentence, if the RI difference was too high or if the mass spectra did not match between the non-target compound and the proposed molecule, the peak could not be tentatively identified. This was made more clearer in the revised version and the sufficient confidence part was removed.

ACM: "If an unknown compound could not be tentatively identified (either too high RI difference or not adequately matching mass spectra), a proposed compound formula was deduced based on the mass spectra.."

### Page 8 line 233-5: if you can't identify the compounds then remove them from identified compounds.

AR: They were considered to be *tentatively identified* since no pure standards of the non-target compounds were available. Hence, it was emphasized that the compounds were not *absolutely identified*. To clarify, for example in the pine needle emissions rimuene was tentatively identified based on both the mass spectra and RI matches, but since we did not have rimuene as pure compound, we cannot declare it to be absolutely identified. This is a common procedure in non-target analysis, the compounds are declared to be tentatively identified. This was corrected and made clearer. References were added to support the procedure used here. In addition to changes made in Section 2.5, the terminology used in Section 3.2 was checked and revised accordingly.

#### ACM: In Section 2.5 the first paragraph was rewritten:

"The non-target compounds in real sample applications were tentatively identified based on both retention index (RI) values and mass spectra comparison to NIST mass spectral library and/or Adams (2007) library. The n-alkane based RI values were calculated based on both Kovats Index (KI) and Arithmetic Index (AI) as shown in Adams (2007). If an unknown compound could not be tentatively identified (either too high RI difference or not adequately matching mass spectra), a proposed compound formula was deduced based on the mass spectra. The non-target compounds that were either tentatively identified or assigned with a formula were then categorised as MTs, SQT and DTs when applicable, the others were categorised as BVOCs. For example, if the non-target compound had the characteristic m/z 272, 257, 243 and 229 ions of DTs and the RI value was representative of DTs (Adams, 2007), the compound was assigned in this study to the plausible DT category. Similar identification procedure of non-target compounds has been used also in previous BVOC studies (e.g. Chan et al., 2016; Hellén et al., 2018; Kännaste et al., 2013; Yee et al., 2018). The compounds were marked here as tentatively identified since authentic standards were not available, thus the final verification is lacking. The analysed blank samples were used to exclude possible contaminant peaks."

In Section 3.2. in three places the wording "positively" was replaced with "tentatively", since even though cembrene (one of our standard analytes) was among the compounds identified in emissions, the others cannot be declared positively identified. The term "unidentified" was changed to "unknown" in the revised Figure captions.

#### Page 8 line 241: What is C1?

AR: This should have been C<sub>in</sub> as marked in the emission rate equation. Now corrected.

ACM: "In both real sample applications, the C<sub>in</sub> was negligible..."

#### Page 8 line 348-9. Remove this sentence, it does not contribute anything to the ms.

AR: Done.

ACM: Sentence removed.

#### Page 9 line 250: what is the desorption efficiency of TDGCMS2?

AR: Information was missing, this was added.

ACM: "With the TD-GC-MS2 desorption time needed to be increased from 1 min to 5 min at 300 °C (both sorbent and cold trap) to minimise the carryover, which arise either from the sorbent tube or cold trap, and to obtain sufficient desorption efficiency ( $\geq$ 99.7%)."

#### Page 9 line 251: what do you mean by carryover?

AR: Here it is meant either the carryover from the sorbent tube or from the other parts of the instrument, likely the cold trap. This information was added.

ACM: "...to minimise the carryover, which arise either from the sorbent tube or cold trap, and to obtain sufficient..."

### Page 9 line 269: why did you choose 60 and not 70 or 50C? How did you know all liquid goes into the gas phase?

AR: This temperature (60 °C) was considered and later observed to being adequate for improving the volatilization of DTs. We didn't test higher temperatures in order to avoid possible PTFE contamination peaks. A comment was added related to this.

As it was explained in the manuscript, it was not a requirement that all the analytes are volatilized, since the tests were performed by relative comparison (sampling sorbent tubes before and after the studied setup, Fig. S1). However, as can be seen in Fig. 2a, the theoretical and observed amounts agreed fairly well, thus with most of the compounds the volatilization was close to "complete". This was clarified in the revised version.

#### ACM: The first paragraph of Section 3.1.3 was revised:

"In Fig. 2a are shown the amount of each compound detected in the first sorbent tube (after the mixing line, Fig. S1a) and the expected theoretical amount calculated based on the experimental conditions used. As can be seen in Fig. 2a, the observed amounts were mostly in close agreement with the expected amounts. Although this was not a prerequisite for the recovery experiments, the relative recovery was calculated based on amounts found in tubes before and after the sampling line, it demonstrates that the experimental setup was working adequately in practice (although the reproducibility was a bit poor for some compounds, see Fig. 2a). The injection t-piece needed to be heated to 60 °C in order to increase the volatilisation of the diterpenes. If there was no heating applied, then e.g. ent-kaurene yield in the first tube was less than 20 % of the expected amount (data not shown). The diterpenes were observed to stick into the walls of the injection PTFE t-piece if it was not heated, thus heating is recommended to be used in similar experiments. Higher temperatures were not tested here in order to avoid the possible PTFE contamination peaks."

### Page 9 line 271: how did you observe that diterpenes were sticking into walls and not decomposing some other way?

AR: This was observed in the preliminary tests and in operational error situations. For example, in the preliminary tests we did not use heating of the injection t-piece. Afterwards when heating was applied, the amounts of DTs detected in the first tests were in great excess demonstrating the sticking into the walls (the DTs that had not volatilized when the t-piece was not heated were now volatilized). In addition, the fact that the recoveries were good indicate that the DTs were not decomposing in any other ways. Another clue that indicates that the DTs were not decomposed in other ways was that no decomposition products were detected in the chromatograms where otherwise DTs were absent.

Since this information is not really required to be explained in the manuscript and it would disturb the flow of the text, no changes were made.

Page 9 line 273-279: This is a very serious statement which I think is wrong. It is fine that you did not find any losses with you inlet line, but this will be highly dependent upon the ambient temperature that the line will be subjected to. For instance 15 m non heated Teflon line for outdoor sqt monitoring in a boreal ecosystem during winter HAS to be heated!. Please remove statement about not heating the Teflon tube, it is totally misleading.

AR: Yes, the referee is absolutely right that this statement was too generalizing. It was not our intention to mean that the non-heated line could be used e.g. in cold season measurements. This part related to field measurement of the sentence was removed. The remaining sentence was modified.

ACM: "The results indicate that under the applied conditions the Teflon FEP sampling lines do not need to be heated excessively above room temperature (22±1 °C)."

Page 9-10 lines 280-297: I wonder what will be the effect of transpiration inside a cuvette. This must be really important for diterpenes as you mention, so I think it is wise to let people know that inside cuvette humidity monitoring is essential.

AR: We added recommendation on humidity monitoring later in Section 3.1.5.

ACM: A sentence on this was added: "Since the RH was shown to have an effect on the recoveries, humidity monitoring of the sample air stream is recommended."

Page 10 line 288-290: why do you think there is a longer residence time in the cuvette for diterpenes? I think this whole paragraph needs to be rewritten. You simply say that you may not be volatilizing well your diterpenes, thus, you can't be really validating the method if you are not sure you can't get all your diterpenes into the gas phase. Please rephrase by 1) taking away the mt and sqt info (because as you say it is explained in other studies) 2) you think account for this HUGE limitation and how this affects your method validation. In fact, somewhere in the text you must state why you are truly validating a method here with these limitations.

AR: It is not stated that the residence time is longer only for DTs. The residence time inside the cuvette is longer for all the compounds at 1 L/min flow rate than at 6.7 L/min flow rate. It was meant that since the recoveries of DTs were worse at 1 L/min flow rate (recovery=44%) than at 6.7 L/min flow rate (recovery=76%), likely the residence time inside the cuvette was too long for these low volatility compounds. The recoveries of MTs and SQTs did not change much between the different flow rates

tested. (Please note that this is an example of results where the information obtained based on MTs and SQTs is very useful for interpreting the DTs results.)

As it was explained in the manuscript, it was not a requirement that all the analytes are volatilized completely since the recoveries were calculated by comparing the concentrations observed before and after the studied setup (in this case a cuvette, Fig. S1c). The problem of volatilization is not in our analytical method, it is in the experimental setup used for testing and it is caused by the physicochemical properties of the target analytes.

To clarify, the problem is this cuvette recovery testing setup was two-phase:

- If high flow rate was used, the heating of the injection t-piece was not efficient enough to maintain the same volatilization efficiency as with the low flow rates. Thus, much lower than expected amounts were detected (in the sorbent tube prior to cuvette, amount shown in Fig. \$10)
- If low flow rate was used, the volatilization of DTs was adequate (the amount observed in the sorbent tube prior to cuvette was closer to expected amount), but the recoveries of DTs were poor.

To make it clearer, we raised the cuvette recovery results figure from the supplementary information to the manuscript. This new Fig. 3 in the revised manuscript likely helps to follow the results more easily and will help the reader in interpreting the results. In addition, the paragraph was modified and rephrased.

ACM: Figure was raised from the supplementary information to help the reader, now it is Fig. 3. Section 3.1.3 last paragraph modified/rephrased:

"The cuvette recovery results showed some variability (Fig. 3). As mentioned in Sect. 2.3.3, three different flow rates were tested (inlet flows 6.7, 2.0 and 1.0 L min-1). The recovery values were acceptable at all flow rates tested for all other compounds except for the diterpenes (Fig. 3). The recoveries of MTs and SQTs were on average 95±1 % and 94±2 % at 1.0 L min-1 and 96±1 % and 93±3 % at 6.7 L min-1 flow rates, respectively. However, the recoveries of DTs were on average 44±11 %, 80±6 % and 76±4 % at flow rates of 1.0, 2.0 and 6.7 L min-1. The poor recoveries of DTs observed at the lowest flow rate tested indicate that the residence time inside the cuvette was likely too long for these low volatility compounds (note that for MTs and SQTs the recoveries were acceptable). The DT recoveries were seemingly adequate with the other flow rates tested, indicating that the set flow rate range of ca. 2–7 L min-1 would be suitable for sampling. However, with the highest flow rate tested, the absolute mass concentrations of DTs were very close to LOQ values (Fig. 3). This was likely related to an experimental problem in the analyte volatilisation setup. The injection t-piece heating was not efficient enough for allowing complete volatilisation of the DTs, since the high flow rate rapidly cooled the t-piece. Therefore, these DT cuvette recoveries need to be considered as tentative results, since the concentrations levels were not systematic between the different flow rates tested (Fig. 3). A better sample introduction system would be needed to get the volatilisation more systematic at all flow rates under investigation."

### Page 10 line 299. I do not understand how you say first that you can't really be sure of 3MA and then you actually show LOQ values. How is this possible?. Please explain.

AR: This is a good question and something that we struggled a bit with during the experimental planning of this work. As it was shown in Table S1, the 3-MA was a crude standard (purity documentation was separately asked from the supplier, but apparently it has not been determined for this chemical). Since the purity was not declared, we simply assumed that all that was weighted in primary standard was pure compound. Thus, we can state the LOQ, but the uncertainty is unknown.

Including the LOQ was considered to be useful information for comparative purposes (both for others planning to reproduce our work and for comparison to MT and SQT results).

ACM: In the revised manuscript in revised Table 1, a footnote was added to 3-MA and in that it was stated: "The purity of this crude standard was set to being 100% (allowing the determination of LOQ, but unknown uncertainty).

### Page 10 line 300: please state that RSD means relative standard error. I wonder why you did not show any repeatability among different systems. This will really validate your method!

AR: Error bars are shown in all the plots presented in the manuscript, and in those plots the error bars correspond to either repeatability or reproducibility (these are already stated in the figure captions). Intermediate precision was used in the calculation of expanded measurement uncertainty.

ACM: "...for all compounds (relative standard deviation, RSD<5 %)..."

#### Page 10 line 306: What do you mean by assuming sampling volume? You must know this.

AR: Yes, the sample volume is known exactly. The LOQ values were also shown in pptv units to represent ambient application and for that purpose a sample volume of 5 L was used. This sample volume would be reasonable in outdoor ambient air measurements. Obviously, as the referees' comment shows, the word "assuming" was not suitable for this and that was changed to "using". Anyone can calculate the LOQ in pptv units themselves since we provide the LOQ in absolute amounts (mass in nanograms in sorbent). The same correction was made in the Conclusions section.

ACM: In Section 3.1.4: "When converted to pptv units by using a sampling volume of 5 L..." In Conclusions section: "If using a sample volume of 5 L in offline sampling,..."

#### Page 11 line 327-9: I do not understand this sentence. Please rephrase.

AR: This was revised. The original sentence was poorly and wrongly written. Please note that the details to these results are given in the supplement Text S2 as written at the beginning of Section 3.1.5.

ACM: "Interestingly, a substantial portion of the compound losses could be explained by the losses onto the empty tube used in online sampling, e.g. the amount of  $\beta$ -farnesene lost in the empty tube was ca. 44%. However, simultaneously a substantial portion of the losses could not be explained by losses onto the empty tube, e.g. up to 98% of the ent-kaurene losses could not be accounted for."

### Page 12 line 375. Please expand on why heated stainless steel better than other ozone removal mechanisms.

AR: Discussion and references on ozone removal techniques was added

ACM: This part was added "Several different kind of ozone traps and filters have been used to trap ozone, but most of them are not suitable even for MTs and SQTs (Polmann et al. 2005, Calogirou et al. 1996). In addition, some of the ozone removal techniques have very short ozone removal capacity and they have to be changed frequently and therefore are not ideal for online sampling (Bouvier-Brown et al. 2009, Fick et al., 2001)."

The following references were added to the manuscript:

Calogirou, A., Larsen, B.R., Brussol, C., Duane, M., Kotzias, D., 1996. Decomposition of terpenes by ozone during sampling on Tenax. Analytical Chemistry 68,1499-1506.

Fick, J., Pommer, L., Andersson, B., Nilsson, C., 2001. Ozone removal in the sampling of parts per billion levels of Terpenoid compounds: an evaluation of different scrubber materials. Environmental Science and Technology 35, 1458-1462.

#### Page 13 line 380. I think it would be wise and enriching the ms if you add this data.

AR: These were preliminary experiments and performed with another GC-MS by using liquid injection. Including this preliminary screening data would not be very informative for the reader. We did not have the alkane series at the time, so even tentative identification was not attempted (only the mass spectra (m/z 272 ion specifically targeted) and the retention time expected range was evaluated for screening of the DTs). The main point in this part was to demonstrate why the birch leaves were not studied any further in the headspace experiments (no DTs could been detected in the birch solute extracts). Since the literature reference Kanerva et al. (2008) corroborated our findings, there was no apparent reason to show the data.

In principle, since this does not contribute significantly to the manuscript, all information regarding the study of birch leaves was excluded from the manuscript. Upon revision, it was considered that the information about birch leaves and DTs was not crucial, although it could have been valuable for future studies. Nonetheless, to avoid prolonging the manuscript/supplement, this information was removed.

ACM: The Section 3.2 first paragraph (starting "Prior to the dynamic headspace extraction...") of the original manuscript was removed. In addition, the mentioning of birch leaves was removed from all parts of the revised manuscript (removed from Section 2.4 and Conclusions).

#### Page 13 section 3.2.1. Please explain why you heat needles and twigs.

AR: Explanation to this has been added in the revised manuscript. This is part of the same corrections as presented earlier in these author replies.

#### ACM: In Section 2.4:

"...The main emphasis on real sample applications was set on the identification and study of DTs, although MTs and SQTs were also monitored. Based on previous studies, it was considered that since the DTs seem to be emitted from plant storage pools and since temperature has been shown to be a driving force for DTs emissions (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018), heating of the plant materials would be an efficient way for releasing the DTs into gas-phase. Thus, the studied plant material samples were firstly heated to temperatures ranging from 30 °C to up to 70 °C in order to obtain presumably detectable amounts of DTs to allow their identification and quantification."

#### In Section 3.2 the following was added:

"As explained in Section 2.4., in the following experiments the plant material samples were heated in order to characterize the DTs potentially emitted by the studied tree species and to further test the TD-GC-MS method performance in view of real sample analysis. The plant material samples were heated to facilitate the release of DTs from the plant storage pools into the gas-phase."

#### Page 13 line 389. If you could only identify 5 how can you report 11?

AR: Five out of the 14 detected compounds could be tentatively identified based on both mass spectra and RI matches. For the other nine detected compounds we proposed a chemical formula and compound group based on the mass spectra (and by sanity checking that the RI was reasonable for that formula). This is explained in Section 2.5 (see ACM). In this Section 3.2.1, a misplaced term "positively identified" was replaced with "tentatively identified". Maybe this was causing the confusion originally.

#### ACM: Revisions in Section 2.5:

"...If an unknown compound could not be tentatively identified (either too high RI difference or not adequately matching mass spectra), a proposed compound formula was deduced based on the mass spectra. The non-target compounds that were either tentatively identified or assigned with a formula were then categorised as MTs, SQT and DTs when applicable, the others were categorised as BVOCs. For example, if the non-target compound had the characteristic m/z 272, 257, 243 and 229 ions of DTs and the RI value was representative of DTs (Adams, 2007), the compound was assigned in this study to the plausible DT category. Similar identification procedure of non-target compounds has been used also in previous BVOC studies (e.g. Chan et al., 2016; Hellén et al., 2018; Kännaste et al., 2013; Yee et al., 2018). The compounds were marked here as *tentatively identified* since authentic standards were not available, thus the final verification is lacking..."

#### Revisions in Section 3.2.1:

e.g. "Of these 14 compounds, only five could be tentatively identified based on mass spectra and retention index matches."

#### Page 13 line 406: what do you mean by coefficients? Please explain.

AR: Nothing, it is there for no apparent reason.

ACM: Coefficients was removed from the sentence.

### Page 15 line 460: what do you mean by good? This is very vague, good as compared to what. Please expand.

AR: Agreed, this was vague. The sentence was removed. In the revised version, it is replaced directly with the results.

ACM: "The sampling recovery results (15 m long Teflon FEP line, 1 m heated stainless-steel line and a Teflon cuvette bag) were mostly acceptable (within 100±20 %) for all studied compounds. For example, the recoveries of DTs were on average 86±1% and 85±6% when the 1 m heated stainless-steel and 15 m Teflon FEP sampling lines were tested, respectively. These sampling recovery results of DTs were promising, since they demonstrated that the DTs were not lost in excessive amounts in the sampling lines tested."

#### **Editting comments**

#### Page 2 Line 34. OH must go before hydroxyl not before radical.

AR: Corrected by assuming that the Reviewer meant after and not before. In our original version we had it "hydroxyl radical (OH) reactivity". This was changed.

ACM: Corrected to: "...total hydroxyl (OH) radical..."

#### Page 2 line 35: You must explain what VOC is, you only said BVOC before.

AR: Done.

ACM: "...reactivity has been introduced to study indirectly the volatile organic compound (VOC) content..."

### Page 7 line 219: put a before temperature and I suppose you mean that you place the temp sensor in the cuvette not the logger itself, right?

AR: Yes, the sensor was inside the cuvette, not the logger itself. Sentence was rephrased.

ACM: "A data logger with temperature sensor was used for monitoring the cuvette inside temperature."

#### Page 9 line 268: replace "with" with "for". And state which compounds you refer to.

AR: Done by guiding the reader to see the plot.

ACM: "...(although the reproducibility was a bit poor for some compounds, see Fig. 2a)."

References:

Mermet, K., Sauvage, S., Dusanter, S., Salameh, T., Léonardis, T., Flaud, P. M., Perraudin, É., Villenave, É., and Locoge, N.: Optimization of a gas chromatographic unit for measuring biogenic volatile organic compounds in ambient air, Atmos. Meas. Tech., 12, 6153-6171, doi:10.5194/amt-12-6153-2019, 2019.

We thank the reviewer #2 for the evaluation of the manuscript. The manuscript was revised according to the reviewers' comments. Here the point-by-point answers are given. The reviewers' comments are in bold and our answers are in normal font. The answers are divided into author's response (AR) and author's changes to manuscript (ACM).

#### Anonymous Referee #2 Received and published: 4 March 2020

The study by Helin et al. describes in depth the analytical method of a thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) to quantify a series of Biogenic Volatile Organic Compounds (BVOC). While the core analytical method has been previously used extensively, such a detailed description of the processes and parameters affecting the sampling collection is a valuable addition. The authors focus their investigations to diterpenes, a highly understudied class of compounds that exhibits difficulties in quantification due to their volatility, low abundance, sticky nature and experimental artefacts. The paper reads well but few critical points deserve more attention. Therefore, the paper is suitable for AMT and I could recommend publication but only after addressing the following comments/concerns.

#### **General comments**

1. There seems to be a confusion on the terminology that starts from the title itself and extends to various points of the text. Terpenes are a class of compounds that include monoterpenes, sesquiterpenes and diterpenes. However, it's true that in the literature terpenes and terpenoids are frequently used in the same bases. But monoterpenoids, sesquiterpenoids and diterpenoids are actually modified terpenes, with different chemical formulas (eg. Chan et al., 2016). I would recommend changing the title to the more general "Biogenic Volatile Organic Compounds" or "Terpenoids". Consequently, individual corrections on the text over case-based referral to the individual species is needed.

AR: We agree with the Reviewer that in the literature a somewhat mixed use of terpenes and terpenoids is unfortunately common. In the revised manuscript we have changed the naming and added to all Tables the compound categories to which we refer to. This helps the reader to trace all the compounds to which we are referring to. In addition, we changed the referred title part to "...monoterpenes, sesquiterpenes and diterpenes". This was considered to being more representative of the main work.

ACM: The terminology has been changed throughout the manuscript. As an example, the compound categories were added Section 2.1. and Table 1: "The analyte included nine MTs (both hydrocarbon and oxygenated MTs), six SQTs (both hydrocarbon and oxygenated SQTs), three diterpenes (all hydrocarbon DTs) and three other compounds that were categorised here as BVOCs."

Revised Table 1:

						Repea			
Compound	CAS Number	Formula	RIª	Quan -tify m/z ion	LOQ in pg (in pptv) <sup>b</sup>	tabilit y (RSD %)	Inter- mediate precision (RSD%)	U <sup>c</sup> (% )	U <sup>d</sup> (%)
α-Pinene (MT)	7785-70-8	$C_{10}H_{16}$	945 (942)	93	34 (1.2)	2.6	3.8	16	18
camphene (MT)	79-92-5	$C_{10}H_{16}$	963 (960)	93	14 (0.5)	1.6	4.0	16	18
β-pinene (MT)	19902-08-0	$C_{10}H_{16}$	989 (988)	93	13 (0.5)	4.2	3.2	17	20
3-carene (MT)	498-15-7	$C_{10}H_{16}$	1018 (1017)	93	18 (0.6)	2.0	3.3	16	17
<i>p</i> -cymene (MT)	99-87-6	$C_{10}H_{14}$	1033 (1031)	119	20 (0.7)	2.0	4.2	17	19
limonene (MT)	5989-54-8	$C_{10}H_{16}$	1039 (1037)	68	62 (2.2)	1.5	3.8	17	17
1,8-cineol (MT)	470-82-6	$C_{10}H_{18}O$	1044 (1042)	154	27 (0.9)	2.6	4.7	18	20
terpinolene (MT)	586-62-9	$C_{10}H_{16}$	1094 (1093)	121	65 (2.3)	2.5	5.0	17	18
linalool (MT)	78-70-6	$C_{10}H_{18}O$	1100 (1100)	71	88 (2.8)	2.4	4.8	18	18
4-acetyl-1- methylcyclohexene (4-AMCH) (BVOC)	6090-09-1	$C_9H_{14}O$	1140 (1139)	95	120 (4.2)	2.7	6.3	19	20
nopinone (BVOC)	38651-65-9	C <sub>9</sub> H <sub>14</sub> O	1154 (1153)	83	29 (1.0)	2.7	5.3	18	21
bornylacetate (BVOC)	5655-61-8	C <sub>12</sub> H <sub>20</sub> O 2	1295 (1294)	95	49 (1.2)	2.4	6.2	20	23
longicyclene (SQT)	1137-12-8	$C_{15}H_{24}$	1401 (1401)	94	35 (0.8)	2.4	4.9	18	21
isolongifolene (SQT)	1135-66-6	$C_{15}H_{24}$	1422 (1422)	161	38 (0.9)	2.5	5.7	19	22
β-caryophyllene (SQT)	87-44-5	$C_{15}H_{24}$	1445 (1444)	93	105 (2.5)	2.2	3.5	17	22
β-farnesene (SQT)	18794-84-8	$C_{15}H_{24}$	1457 (1456)	69	198 (4.7)	5.0	5.9	20	22
α-humulene (SQT)	6753-98-6	$C_{15}H_{24}$	1481 (1480)	93	33 (0.8)	2.1	4.2	18	24
caryophyllene oxide (SQT)	1139-30-6	$C_{15}H_{24}O$	1612 (1612)	79	340 (7.5)	18.9	8.6	24	28
cembrene (DT)	1898-13-1	$C_{20}H_{32}$	1959 (1959)	93	287 (5.1)	4.0	9.5	27	52
ent-kaurene (DT)	562-28-7	$C_{20}H_{32}$	2106 (2106)	257	518 (9.3)	2.9	7.7	26	42
3-methylene-5-α- androstane (3-MA) <sup>e</sup> (DT)	not assigned	$C_{20}H_{32}$	2153 (2152)	257	383 (6.9)	3.0	7.2	-	-

Table 2. List of analytes, corresponding retention indices (RI) and analytical figures of merit.

<sup>a</sup> RI as Kovats indices (and arithmetic indices in brackets)

<sup>b</sup> LOQ in pptv calculated by using sample volume of 5 L (at T=298 K and p=1 atm)

<sup>c</sup> U (%) for ambient air application

<sup>d</sup> U (%) for branch enclosure application

<sup>e</sup> The purity of this crude standard was set to being 100% (allowing the determination of LOQ, but unknown uncertainty)

2. My most serious concern has to do with the striking claim that there is no need for heating the Teflon lines in field applications, in contrast to almost all experimental approaches in the field to date. That conclusion was derived performing sampling recovery tests over which a second sample was taken subsequent to the original (L159: "Inlet line recovery was calculated simply by the relationship of analytes found in the second tube divided by the amounts in the first tube.") One would naturally expect that when the line is kept at the same temperature, artifacts cannot be evaluated properly. The losses on the line could be better illustrated if after the first sample, a subsequent "blank" sample over a now heated line is taken. In this approach, the amount of VOCs stuck in the tube could be quantified and the proper temperature for heating up the lines could be ascertained.

AR: We agree with the Reviewer. The original sentence was too generalizing. It was meant that the Teflon FEP sampling line does not need to be extensively heated. It was not intended to mean that non-heated Teflon FEP lines could be used e.g. during cold spring. We revised this part so that our results better corroborate the statement and removed the field applications part from the sentence. In the revised manuscript there is no claim of non-heated lines usage in field measurements anymore.

ACM: "The results indicate that under the applied conditions the Teflon FEP sampling lines do not need to be heated excessively above room temperature  $(22\pm1 °C)$ "

3. Similar to the previous comment, the authors describe in S1.5 the problems that arise with the replacement of the Teflon line. It seems that a new line is causing more artefacts comparing to a used one, indicating some saturation over the line surfaces. In general, the inlet line experiments should be explained in greater detail. The claim that Teflon lines should remain unheated for field applications has the potential to mislead future research and therefore it cannot become acceptable unless strong and well described proof of concept is presented.

AR: The reviewer is correct. In the original manuscript we had a sentence that was too generalizing, and it could have been interpreted in a wrong way. It was not our intention to mislead the reader. The sentence was modified as shown in above point 2. ACM part.

The inlet line experiments are explained quite thoroughly in Section 2.3.3 and in the schematic illustrations of the setups presented in the supplementary (the information is presented so that others can reproduce the experiments). This was not really expanded, since upon revision, no missing information could be identified. Also, in that Section 2.3.3 another study by Hellen et al. (2012) is cited, where a similar experimental setup was used.

Regarding the Supplementary S2.5 (in the revised version it is Text S2), it is true that the line changes initially caused a drop in the overall recovery levels. The lines and connections were checked a few times to identify leaks, which were thought to be the reason, but we could not verify the leaking for sure. It was left a bit open question was the improvement overtime really caused by the "saturation" as the reviewer puts it or by the done leak checking open/closing connections. Since the leak checking information was not really scientific nor fitted the text, it was not included originally in the S2.5. However, due to this comment, it was considered to being relevant and was added to the supplement text.

Change to supplement: "It is unknown if the initially observed drop in overall recoveries was caused by some active surfaces in the Teflon line (which became saturated over time) or by potential loose connections upon line changes (connections were open/closed separately a few times to investigate possible leaking)." 4. There is a lot of useful information, results and discussion in the supplementary information. Sometimes, it becomes challenging to follow the text while browsing through Figures, Supplementary Figures, additional discussion and references. I would recommend to bring forward the supplementary discussion, including several of the figures.

AR: In the original manuscript, we attempted to keep the main text and figures as compact as possible and to present all complementary information in the supplementary information (SI). We wish to keep it so for the most part. However, in view of one of the Reviewer #1 comments and this comment, the supplementary figure showing the cuvette results was raised from the SI to the manuscript in order to help the reader better transit between the text and the plot for results interpretation purposes. In addition, upon revision, it was considered that the real sample chromatograms could fit in the manuscript and that these could help the reader in visualizing the results, thus those were also raised from the SI to the manuscript.

ACM: Three supplementary Figures were raised to the manuscript (now these are Figs. 3, 6 and 7). The Fig. 3 shows the cuvette recovery results, while Figs. 6 and 7 are the chromatograms from pine needles and spruce twigs extraction experiments, respectively (revised by adding blank chromatograms also to those).

5. In order to derive some quantitative emissions of diterpenes from needles, the experiments (both in lab and field) were performed under unrealistically high temperatures. While this is acceptable for validating the method, it should be further noted that these are stored compounds coming for the pools of the plant material and further highlight the reasons for this approach. Some investigations between the vapor pressure and measured emissions would be nice addition to the paper, if possible.

AR: Thank you for pointing this out. The information about the emissions coming from storage pools was added to justify the approach. This was added to Sections 2.4 and 3.2. (related also to Reviewer #1 comments).

In general, we agree with the Reviewer that some investigation between vapor pressure and measured emissions could be nice addition, however, we are not sure how it would fit into this manuscript and what it would contribute eventually to the overall manuscript. As an example, in Figs. AR1 and AR2 are presented the plots of emissions rates as a function of vapor pressures from the pine needles and spruce twigs experiments, respectively. The vapor pressures (in mmHg at 25 °C) were predicted values obtained via EpiSuite (https://www.epa.gov/tsca-screening-tools) and are presented only for those compounds that could be tentatively identified. The emission rates are presented at 30 °C and 60 °C as observed in the laboratory experiments performed in our study (e.g. in Fig. AR1 one of the tentatively identified diterpenes was emitted only at 60 °C, therefore the point is missing from the 30 °C results). In the plots, both x- and y-axis are presented in logarithmic scales.

As can be seen in these Figs. AR1 and AR2, the emission rates are the highest for the most volatile compounds investigated (monoterpenes) and the lowest for the least volatile compounds investigated (diterpenes). In principle, this is a fairly trivial result and does not necessarily tell anything meaningful about, for example, the terpene content of the plant storage pools. There could be also some uncertainty in the predicted vapor pressure values used here. In the end, we decided not to present these plots in the manuscript. In our opinion, the added value would have been minor and it would have not fitted into the main scope of our study.



Figure AR1. Relationship between emission rates (E) and vapor pressure in the emissions from pine needles laboratory experiments.



Figure AR2. Relationship between emission rates (E) and vapor pressure in the emissions from spruce twigs laboratory experiments.

ACM: The beginning of Section 2.4 was rewritten and modified:

"Two types of real sample applications were selected in order to test the analytical method performance, to identify compounds emitted by boreal forest tree species and to quantify the emissions from a branch enclosure. The first sample application was a dynamic headspace sampling of compounds emitted by needles/twigs in a closed chamber upon heating, and the second sample application was a study of emissions from a branch enclosure in field conditions. The main emphasis on real sample applications was set on the identification and study of DTs, although MTs and SQTs were also monitored. Based on previous studies, it was considered that since the DTs seem to be emitted from plant storage pools and since temperature has been shown to be a driving force for DTs emissions (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018), heating of the plant materials would be an efficient way for releasing the DTs into gas-phase. Thus, the studied plant material samples were firstly heated to temperatures ranging from 30 °C to up to 70 °C in order to obtain presumably detectable amounts of DTs to allow their identification and quantification."

In the second paragraph of Section 3.2 the following was added:

"As explained in Section 2.4., in the following experiments the plant material samples were heated in order to characterize the DTs potentially emitted by the studied tree species and to further test the TD-GC-MS method performance in view of real sample analysis. The plant material samples were heated to facilitate the release of DTs from the plant storage pools into the gas-phase."

#### Specific comments

L34-40. The authors probably refer to the comparative reactivity method. If so, the reference of Kovacs and Brune is misplaced. Instead the study by Sinha et al (2008) should be cited.

AR: Yes, it should be Sinha et al. (2008) not Kovacs and Brune.

ACM: Reference Kovacs and Brune removed and was changed to Sinha et al. (2008).

#### L93. Please make a comment on how the commercial adsorbent tubes compare with the custommade ones.

AR: In this work, the commercial and custom-made tubes were used randomly. For example, the intermediate precision (n=22) and blanks (n=10) used for LOQ determination contain results from both types of tubes. This information was added.

ACM: "The commercial and in-house prepared tubes were used collectively and randomly in this work."

## L154-155. Zero air generators and carbon cartridges have frequently shown that are not completely scrubbing the VOCs. Have you tested the efficiency of these methods? How do they compare between them?

AR: In our case both purification systems worked fine for our purpose, at least they scrubbed the BVOCs we were investigating. In this work, we did not compare the different purification setups.

This is said in the manuscript in Section 2.5: "In both real sample applications, the  $C_{in}$  was negligible (or <LOQ) for all compounds, and was subsequently set to zero in the calculations."

### L182&L239. Please use equations in separate lines so they are clearly distinguishable from the rest of the text.

AR: Done.

ACM: Equations were added to separate lines.

## L375. O3 removal. Have you tested other scrubbers? Why the heated stainless steel in the optimal solution of ozone removal and not e.g. KI scrubbers or Na2S2O3 infused quartz filters? Please refrain from strong claims that are not supported by experiments.

AR: Discussion and references on ozone removal techniques was added. Changes were made to avoid too strong claims, e.g. the "optimal solution" was replaced with "good solution".

ACM: This part was added "Several different kind of ozone traps and filters have been used to trap ozone, but most of them are not suitable even for MTs and SQTs (Polmann et al. 2005, Calogirou et al. 1996). In addition, some of the ozone removal techniques have very short ozone removal capacity and they have to be changed frequently and therefore are not ideal for online sampling (Bouvier-Brown et al. 2009, Fick et al., 2001)."

In addition the sentence was modified a bit "Based on the ozone removal results presented in Hellén et al. (2012) and the inlet recovery results presented in this study (Fig. 2d), heated stainless-steel line could be a good solution for ozone removal especially in online sampling." to avoid too strong claims.

#### The following were added to References:

Calogirou, A., Larsen, B.R., Brussol, C., Duane, M., Kotzias, D., 1996. Decomposition of terpenes by ozone during sampling on Tenax. Analytical Chemistry 68,1499-1506.

Fick, J., Pommer, L., Andersson, B., Nilsson, C., 2001. Ozone removal in the sampling of parts per billion levels of Terpenoid compounds: an evaluation of different scrubber materials. Environmental Science and Technology 35, 1458-1462.

#### L386. Please make a comment on the saturated peaks of Sup.Fig.19-20.

AR: Those are not saturated peaks, the chromatograms are just scaled in such a way that all the peaks are visible. The comment clarifying this is present in the respective captions, e.g.: "The chromatogram is scaled for presentation purposes, peak number 3 is not showed in full height in order to visualize the other peaks more clearly." These Figures are now in the manuscript, Figs. 6 and 7. No changes were made regarding this since the information is in the captions.

L463. Similar to my major comments, it has not been sufficiently demonstrated that the ambient sampling DTs does not require heating lines. One potential experiment to help towards this direction would be to sample through a long inlet line the analyte mixture at different temperatures and present a plot of inlet temperature vs signal.

AR: This sentence was removed and the paragraph was revised. The last sentence of the paragraph was changed.

ACM: "These sampling recovery results of DTs were promising, since they demonstrated that the DTs were not lost in excessive amounts in the sampling lines tested."

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# Development of a thermal desorption-gas chromatography-mass spectrometry method for the analysis of monoterpenoidsterpenes, sesquiterpenoidsterpenes and diterpenoidsterpenes

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Abstract. In this study, a thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) method following sorbent tube sampling was developed for the determination of monoterpenoidsterpenes (MTs), sesquiterpenoidsterpenes (SQTs) and diterpenoidsterpenes (DTs) in gas-phase samples. The analytical figures of merit were determined, and the method performance was tested by conducting experiments related to, for example, sampling recovery, storage stability and<sub>7</sub> ozone reactivity and general method validation. The limit-of-quantification values were 13–518 pg (0.5–9.3 pptv), intermediate precision was in the range of 3–10 % and the expanded measurement uncertainty was in the range of 1<u>67–40–55</u>% for terpenoidsterpenes. The sampling recoveries of terpenoidsterpenes were approximately within 100±20 % with different inlet lines (15 m long Teflon and 1 m long heated stainless-steel) and branch enclosure cuvette (6 L Teflon bag) tested. Ozone is an

- 15 important factor causing losses of the studied compounds during sampling. Therefore Therefore, losses of terpenes with differentupon ozone exposure s-werewere studied and the reaction rate coefficients were estimated. The ozone reaction rate coefficient ( $k_{03}$ ) of ent-kaurene was experimentally estimated to be 2 orders of magnitude greater than the respective literature  $k_{03}$  value, demonstrating the potential underestimation of DTs contribution to atmospheric reactivity. The preliminary comparison between offline and online mode TD-GC-MS sampling and analysis revealed that diterpenes and oxygenated
- 20 sesquiterpenes are lost in excessive amounts in online mode sampling, hindering the online mode applicability for the quantitative analysis of these compounds. A few applications to real samples were tested to identify DTs potentially emitted by boreal forest tree species. In dynamic headspace samples of pine needles and spruce twigs heated to 60 °C, five <u>DTs</u> and 13 DTs could be detected in emissions, respectively. The semi-quantitatively estimated emission rates of DTs were roughly 1 to 3 orders of magnitude lower than those of MTs and SQTs. Similarly, in spruce branch enclosure emissions from a living
- 25 tree, seven-six\_DTs were detected once the enclosure was heated to ca. 60 °C. In summary, the developed analytical method procedure was demonstrated to be applicable for the analysis of MTs, SQTs and DTs. In addition, DTs could be detected in needles, twigs and branch enclosure emissions, however, high temperatures were required to promote the emissions and for obtaining detectable concentrations.

#### **1** Introduction

- 30 Biogenic volatile organic compounds (BVOCs) are directly emitted from the biosphere into the atmosphere. Globally, BVOC emissions are estimated to reach ca. 760 Tg (C) yr<sup>-1</sup> and chemically consist mainly of isoprene, monoterpenoidsterpenes (MTs,  $C_{10}$ ), sesquiterpenoidsterpenes (SQTs,  $C_{15}$ ), methanol and acetone (Guenther et al., 1995;Guenther et al., 2012;Sindelarova et al., 2014). Most of the emitted BVOCs have high reactivity in the atmosphere and their lifetimes vary from minutes to hours (Atkinson and Arey, 2003). Therefore, they strongly affect the oxidative capacity of the atmosphere both regionally and
- 35 globally. In the reactions, BVOCs form less volatile compounds and participate in secondary organic aerosol (SOA) formation, thus also affecting Earth's radiative budget (Ehn et al., 2014;Hoffmann et al., 1997;Jimenez et al., 2009). During the last decade, a new technique to measure atmospheric total hydroxyl (OH) radical (OH) reactivity has been introduced to study indirectly the volatile organic compound (VOC) content of the atmospheric air (Kovaes and Brune, 2001;Yang et al., 2016)Sinha et al., 2008; Yang et al., 2016). By measuring how much OH radicals are consumed in the
- 40 reactions and by comparing this amount with the known amount of VOCs obtained from chemical composition measurements, it can be evaluated how much unknown reactive compounds there are in the atmosphere. Several studies have shown that the gap between known and unknown compounds can be fairly large (Yang et al., 2016), for example, in boreal forest the missing fraction is approximately 50 to 90 % (Nölscher et al., 2012;Praplan et al., 2019;Sinha et al., 2010). Therefore, there is a need to identify compounds responsible for this missing atmospheric OH reactivity.
- 45 Terpenoids, mostly isoprene\_(C<sub>5</sub>H<sub>8</sub>)-and MTs-(C<sub>10</sub>H<sub>16-18</sub>O<sub>0-1</sub>), have been studied quite intensively during past decades in boreal forest areas (Eerdekens et al., 2009;Hakola et al., 1998, 2003, 2009;Kontkanen et al., 2016;Rinne et al., 2007;Vanhatalo et al., 2018). While there are also studies on SQTs-(C<sub>15</sub>H<sub>24</sub>O<sub>0-1</sub>) (Hakola et al., 2001, 2006, 2017;Hellén et al., 2018;van Meeningen et al., 2017;Yassaa et al., 2012), no atmospheric observations of diterpenoidsterpenes (DTs, C<sub>20</sub>H<sub>32-34</sub>O<sub>0-1</sub>) yet exist in the boreal forest areas. However, DTs have been found in essential oils of some boreal forest tree species (Judžentienė
- 50 et al., 2006;Kanerva et al., 2008;Kupcinskiene et al., 2008;Tumen et al., 2010), for example, in Scots pine needles grown in northern Europe the DTs comprised 6–14 % of the essential oil content (Judzentiene and Kupcinskiene, 2008). Even though diterpenoidsterpenes have not been detected (or *specifically* studied) in boreal forest air, they have been recently observed in atmospheric air and branch enclosure emissions in other environments (Chan et al., 2016;Haberstroh et al., 2018;Li et al., 2019;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018;Yee et al., 2018). For example, at a rural site in Brazil the mean
- concentrations of DTs in air varied between 10–86 ppqv (Yee et al., 2018), and in Mediterranean gum rockrose enclosure the emission rates of DTs were in the range of  $8 \times 10^{-5}$ – $14 \times 10^{-5} \mu g g^{-1} h^{-1}$  (Haberstroh et al., 2018). Therefore, it could be that DTs are one of the compounds included in the missing OH reactivity group. In addition, DTs are potentially contributing in secondary organic aerosol formation (Yee et al., 2018).

Diterpenes have fairly low vapor pressures and they can be categorised as semi- or low-volatile volatile-organic compounds.

60 <u>The determination of DTs in atmospheric gas-phase samples can be challenging due to their low-volatility and high reactivity</u>, which might cause sampling line losses and emphasize the need for high-sensitivity detection methods (Yáñez-Serrano et al.,

<u>2018;Yee et al., 2018).</u> -(SVOCs).- In previous atmospheric studies, DTs <u>and their derivatives</u> have been analysed by using either conventional chromatographic techniques or online mass spectrometric techniques (such as proton-transfer-reaction mass spectrometry) (Chan et al., 2016;Haberstroh et al., 2018;Li et al., 2019;Matsunaga et al., 2012;Yáñez-Serrano et al.,

- 65 2018;Yee et al., 2018). Many of those chromatographic studies <u>targeting DTsused\_used</u> traditional sorbent tubes for sampling prior to thermal desorption (or solvent desorption)-gas chromatography-mass spectrometry (TD-GC-MS)<u>analysis</u> (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018). <u>In general, previously Typically, oo</u>ffline ((and online)) TD-GC-MS <u>methods havetechnique has</u> been mainly used for the analysis of MTs and SQTs (<u>e.g.</u> Hellén et al., 2018;Mermet et al., 2019; Pankow et al., 2012), but the above-mentioned branch enclosure and ambient air studies indicate that this analytical
- 70 technique is also applicable for the analysis of DTs (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018). Unfortunately, most of those studies did not present any any detailed method descriptive validation or performance parameters for DTs (e.g. detection limits, reproducibility, selectivity or sampling recovery), making it difficult to critically evaluate the suitability of the methods-analytical procedures for the analysis of low volatility DTs (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018). –In general, sorbent tube sampling and-followed by TD-GC-MS analysis methods
- 75 methods have been demonstrated to be suitable for the analysis of MTs, however, there is very little detailed information about the suitability for the analysis of SQTs (Bouvier-Brown et al., 2009;Helmig et al., 2004;Jones et al., 2014;Mermet et al., 2019;Pankow et al., 2012), and data related to DTs is currently lacking.

In this study,<u>the applicability of</u> sorbent tube sampling followed by TD-GC-MS analysis for the determination of MTs, SQTs and especially DTs in branch enclosure emissions (and in gas-phase samples in general) was <u>developed and</u> evaluated. The

- 80 TD-GC-MS method was\_partially incorporated from our\_group's previous studies (see e.g. Hellén et al., 2018), and modified accordingly to fit the needs for the analysis of <u>low-volatility</u> diterpenes.\_-In principle,\_<u>the core\_similar</u> analytical method procedures <u>has-have</u> been used previously in both ambient air and enclosure emission studies for the analysis of <u>relatively</u> <u>volatile</u> and <u>semi-volatile</u> MTs and\_SQTs in multiple field campaigns (Aaltonen et al., 2011;Hellén et al., 2018;Joensuu et al., 2016;Mäki et al., 2017;Vanhatalo et al., 2018). In this work, we build on our previous knowledge of the TD-GC-MS technique
- 85 and developed our core TD-GC-MS method further to allow the analysis of the fairly low-volatility DTs. -In this study, the method development and applicability related experiments done in view for the analysis of DTs included e.g. desorption efficiency, sampling recovery, stability tests, comparison of online and offline sampling modes and ozone reactivity tests. The method analytical figures of merit were also determined, including the quantification limits, intermediate precisions and measurement uncertainties for the terpenes. In addition to method performance experiments, qualitative and semi-quantitative
- 90 experiments were conducted in laboratory and in field conditions to characterise the DTs potentially emitted by boreal forest tree species.

#### **2** Experimental

#### 2.1 Chemicals and materials

Detailed information on chemicals is presented in the Supplement Table S1. The standard analytes list is presented in Table 1.

- 95 The analytes analyte included nine MTs (both hydrocarbon and oxygenated MTs), six SQTs (both hydrocarbon and oxygenated SQTs), three diterpenes (all hydrocarbon DTs) and three other compounds that were categorised here as BVOCs. Unfortunately, only three commercially available DTs were obtained for this study and only two of these were analytically valid in terms of purity and traceability (Tables 1 and S1). The current supply (and to some extent price) situation of DTs is not optimal for the purpose of comprehensive method development, however, together with the results of MTs and SQTs to compare to, valuable information was expected be obtained even with only few DTs included as analytes.
- Primary standard <u>mix</u> solutions of the target compounds were prepared by weighting and diluting the pure compounds with <u>in</u> methanol. The analyte concentrations in primary solution were <del>approximately in the range of 40–200</del> mg L<sup>-1</sup> <u>depending on the</u> <u>compound</u>. Six calibration standard solutions were prepared by pipetting appropriate amount of primary solution and diluting with methanol. The standard solution concentrations ranged from 40–200  $\mu$ g L<sup>-1</sup> (lowest standard) to 8000–40000  $\mu$ g L<sup>-1</sup>
- 105 (highest standard). The primary and standard solutions were stored in the dark at 4 °C. The stainless-steel multiphase adsorbent (Tenax TA/Carbopack B) tubes (o.d. 1/4 in. x 3<sup>1</sup>/<sub>2</sub> in.) used in this study were either purchased directly from PerkinElmer Inc. (Waltham, MA, USA) or prepared manually in the laboratory. The in-house packed sorbent tubes were prepared by packing empty stainless-steel tubes (PerkinElmer Inc., Waltham, MA, USA) with Tenax TA (60-80 mesh) and Carbopack B (60-80 mesh), both materials purchased from Sigma-Aldrich (St. Loius, MO, USA). Silanized
- 110 glass wool (Phase Separations Ltd., Deeside, UK), stainless-steel mesh (Markes International, Llantrisant, UK) and gauzeretaining spring (Markes International, Llantrisant, UK) were used to prevent sorbent phase mixing and exiting. The adsorbent tubes were preconditioned at 300 °C for 150 min under helium flow. Prior to each use, the sorbent tubes were always conditioned for a minimum of 10 min at 300 °C. With these sorbent tubes, the sampling flow rate used throughout this study was typically 80–100 mL min<sup>-1</sup>. The commercial and in-house prepared tubes were used collectively and randomly in this work.

The sorbent tubes were also used for TD-GC-MS calibration. Calibration tubes were prepared by injecting 5  $\mu$ L of individual standard solution into the tube and simultaneously applying 80 mL min<sup>-1</sup> flow of nitrogen ( $\geq$ 99.9999 % AGA, Espoo, Finland) as carrier gas for 10 min. The tubes were purged for 10 min in order to evaporate the excess methanol (Hakola et al., 2003). The calibration <u>concentration</u> ranges expressed as absolute amount in sorbent tube-were typically approximately 0.211–55.800 ng

120 for MTs, 0.2<del>10</del>–61.200 ng for SQTs, 0.<u>4350</u>–200.000 ng for DTs and 0.202–43.<u>2</u>200 ng for other BVOCs (expressed as absolute amount (ng) in sorbent tube).

#### 2.2 Thermal desorption-gas chromatography-mass spectrometry

As mentioned before in the Introduction, the TD-GC-MS method used here was partially applied from a previously developed and validated in-house method that has been used in our group's previous studies for the analysis of MTs and SOTs (see e.g.

- 125 Hellén et al., 2012, 2018). In this current work, the analytical GC column stationary phase (nonpolar 1,4-bis(dimethylsiloxy)phenylene polydimethylsiloxane) film thickness was decreased from a previously used thick phase 1.0 μm column to 0.25 μm column as a compromise to maintain proper selectivity between the terpenes and to elute the DTs in reasonable time (chromatograms presented later on). It was expected that the DTs might retain too strongly in the 1.0 μm film thickness column and that the column bleed could become a problem in long-term use since high temperatures are required to
- 130 elute the DTs. Thus, the analytical column was replaced, GC oven temperature program was modified, and the MS scan settings were updated and modified. For the most part, the TD unit parameters' were kept as in the previously optimized in-house method, however, the desorption efficiency was separately tested and verified in this work.

The analyses were performed by using two different thermal desorption-gas chromatography-mass spectrometers (TD-GC-MSs), which are identified and abbreviated hereafter as TD-GC-MS1 and TD-GC-MS2. Most of the analytical method

- 135 development and validation performance tests were conducted with TD-GC-MS1, whereas TD-GC-MS2 was used mainly for real sample applications. The details of both instruments and methods are presented in Table S2 and mentioned here briefly. The TD-GC-MS1 consisted of an automatic TD unit (TurboMatrix 350) connected to a GC (Clarus 680) coupled to a quadrupole MS (Clarus SQ 8 T), all units purchased from PerkinElmer Inc. (Waltham, MA, USA). The cold trap in TD and column in GC were Tenax TA/Carbopack B and Elite-5MS (60 m x 0.25 mm (i.d.), film thickness 0.25 µm), respectively (both
- 140 from PerkinElmer Inc., Waltham, MA, USA). The TD-GC-MS2 consisted of an automatic TD unit (TurboMatrix 650) connected to a GC (Clarus 600) coupled to a quadrupole MS (Clarus 600 T), all purchased from PerkinElmer Inc. (Waltham, MA, USA). In this TD-GC-MS2, the cold trap in TD and column in GC were Tenax TA (PerkinElmer Inc., Waltham, MA, USA) and DB-5MS (50 m x 0.25 mm (i.d.), film thickness 0.25 µm, from Agilent Technologies, Palo Alto, CA, USA), respectively. The main differences with in these TD-GC-MSs were the models of units, different cold traps and columns (same
- stationary phases, but 10 m shorter column in TD-GC-MS2) installed. Also, the TD-GC-MS1 has an online sampling feature in the TD unit (discussed later on), whereas the TD-GC-MS2 can be used only for offline sorbent tube analysis. With both instruments, the optimised offline TD-GC-MS analysis was performed fundamentally in a similar manner, although the duration of different steps differed slightly (for details, see Table S2). Briefly, the sorbent tube was first dry purged in the TD for either 1 min or 5 min at room temperature at a flow rate of 50 mL min<sup>-1</sup> of helium (≥ 99.9996 %, AGA, Espoo, Finland).
- 150 In the primary desorption, the sorbent tube was desorbed for 5 min at 300 °C at a flow rate of 50 mL min<sup>-1</sup> of helium. The desorbed compounds were trapped into a cold trap held at 20 °C during the primary desorption. Then, in the secondary desorption, the cold trap was rapidly heated to 300 °C and held for either 1 min or 5 min. The helium flow rate during the cold trap desorption was either 10 or 30 mL min<sup>-1</sup>, of which 1 mL min<sup>-1</sup> was entering the GC column and rest was passed to outlet split. The temperature of the heated valve in the TD was 220 °C. The heated line temperature between TD and GC was set to

- 155 200 °C. With TD-GC-MS1, the oven temperature program was as follows: 60 °C (held for 2 min), then to 300 °C at 8 °C min<sup>-1</sup> and 300 °C (held for 15 min). With the TD-GC-MS2, the oven temperature program was otherwise similar as with TD-GC-MS1, except the final step 300 °C was held only for 3 min. The flow rate of helium carrier gas into the analytical column was 1.0 mL min<sup>-1</sup> with both instruments. The GC-MS transfer line temperature was 220 °C with both TD-GC-MSs. In MS, electron ionisation at 70 eV was used. Total ion chromatogram (TIC) was scanned in m/z range 50–350 and selected ion recording (SIR) time windows with quantifier and qualifier ions were applied for the target analytes. The selected quantify m/z ions were
- typically base peaks or molecular ion peaks (Table 1).

#### 2.3 Method development and experiments

As mentioned before, the TD GC MS method was applied from a previously developed and validated in house method that has been used in previous studies for the analysis of MTs and SQTs (see e.g. Hellén et al., 2012, 2018). The different experiments done in this study for development and testing the TD GC MS method applicability for the sampling and analysis of diterpenes included, e.g. desorption efficiency, storage stability, sampling recovery, ozone reactivity losses and preliminary comparison between offline and online mode TD GC MS analysis.

#### 2.3.1 Desorption efficiency

Desorption efficiency was tested by doing two consecutive desorptions from the same sorbent tube loaded with analytes (c=40-

170 200 ng). Triplicate measurements were done. Desorption efficiency was calculated by dividing the amount detected in the first desorption by the total amount detected in both desorption cycles.

#### 2.3.2 Stability in storage

The stability of the analytes in sorbent tube (c=40–200 ng) was evaluated by storing the tubes (n=2-6) sealed with brass Swagelok caps and PTFE ferrules at 4 °C in the dark for ca. 1 week (5 days), 1 month (32–33 days) and 2 months (62 days). The stability after storage was compared to sorbent tubes analysed immediately after standard preparation.

#### 2.3.3 Sampling recovery

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The inlet sampling line recovery tests were done by using two different commonly used inlets and at two different relative humidity (RH) levels. The inlet recovery experiments were done in a similar manner as in Hellén et al. (2012). The schematic illustrations of the setups used in the experiments are presented in Fig. S1. Briefly, analyte solution was injected into a zero

180 air stream via a heated (ca. 60±5 °C) Teflon PTFE t-piece by using an automatic syringe pump (at injection flow rate of 15 μL h<sup>-1</sup>). The zero air was produced either by using a zero air generator (HPZA-7000, Parker Balston, Lancaster, NY, USA) or by passing laboratory room air through a carbon cartridge (100 g active carbon from Pall Life Sciences, Ann Arbor, MI, USA). The main flow rate was 0.8–1.0 L min<sup>-1</sup>. The volatilised analytes passed through a 4 m long Teflon fluorinated ethylene

185 second sorbent tube sample was taken after the inlet line under investigation. Inlet line recovery was calculated simply by the relationship of analytes found in the second tube divided by the amounts in the first tube.

The inlets tested were a 15 m long Teflon FEP tubing (i.d. 1/8 in.) and a 1 m long heated stainless-steel (grade 304) tube (i.d. 1/16 in., heated to ca. 150 °C), of which the latter is normally used for ozone removal purposes (Hellén et al., 2012). Both inlet lines tested here are typically used in BVOC studies (Hakola et al., 2017;Hellén et al., 2018). The RH levels were attempted

to control to close to 0 % and 100 % to cover the extremes, but in reality these were roughly 13±5 % (RH=0 %) and 87±6 % (RH=100 %). The RH was measured with a Vaisala HMI 33 device (probe HMP 35, Vaisala, Helsinki, Finland). All experiments were performed at room temperature (T=22±1 °C).

In addition to inlet sampling line recoveries, an enclosure cuvette recovery was tentatively tested. The cuvette was a ca. 6.2 L bag made of Teflon FEP (wall thickness 50  $\mu$ m); similar cuvette has been used previously in branch enclosure studies (Hakola

195 et al., 2017). The cuvette recovery was tested in a similar manner as the inlet line recovery: the first sorbent tube was placed at the inlet end of the cuvette and the second tube at the outlet end of the cuvette (Fig. S1c). Three different flow rate combinations were tested: 1.0, 2.0 and 6.7 L min<sup>-1</sup> at the inlet end and 0.7, 1.7 and 6.4 L min<sup>-1</sup> at the outlet end of the cuvette, respectively. The cuvette bag was not air-tight, so excess flow leaked out freely.

#### 2.3.4 Comparison between online and offline mode sampling

As mentioned earlier, the TD-GC-MS1 has an online sampling feature in the TD unit. In online sampling mode, the air sample is drawn through an empty tube onto the cold trap where the analytes are trapped and preconcentrated. This online mode sampling feature has been used previously in field studies for the analysis of MTs and SQTs, e.g. in Hellén et al. (2018). The online sampling mode was compared to offline sampling mode with the TD-GC-MS1. Known amount of standard solution was injected into a 1.0 L min<sup>-1</sup> flow rate of zero air stream. After a ca. 4 m long Teflon FEP mixing line, both the offline sorbent tube sample (at 100 mL min<sup>-1</sup>) and the online sample (at 40 mL min<sup>-1</sup>) were taken concurrently (for 30 min) as illustrated in Fig. S2. A more detailed explanation of the experiments are presented later on.

#### 2.3.5 Method validationAnalytical figures of merit

The limit of quantification (LOQ) values for the TD-GC-MS method were determined by analysing multiple blank sorbent tubes (n=10). The LOQ was calculated following Eq. (1):

(1)

#### $210 \quad LOQ = A + 10 \times SD,$

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Equation LOQ=A+10\*SD, where A=average peak area and SD=standard deviation, was used for the calculations of LOQ values. Repeatability was calculated by analysing standard samples (n=6) during one day, and intermediate precision (or *reproducibility within-laboratory*) was obtained from analysing standard samples (n=22) during 4.5 months period (c=10-50 ng in sorbent tube). The expanded measurement uncertainty (U) was estimated by from partial uncertainties of the method-by following ACTRIS (Aerosol Clouds Trace gases Research InfraStructure) guidelines (ACTRIS, 2018). The U (%) was

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estimated for two analytical procedures: <u>A more detailed description of the uncertainty calculation can be found as</u> <u>supplementary information.i)</u> offline sorbent tube sampling of ambient air followed by TD-GC-MS analysis and ii) offline sorbent tube sampling of emissions from a branch enclosure cuvette followed by TD-GC-MS analysis. The intermediate precision and recovery experiment results were included in the calculations of U. In the ambient air sampling procedure, the

220 <u>ozone removal inlet recovery results were used in the calculations, whereas in the branch enclosure emissions procedure the cuvette recovery results were used in the calculations. A more detailed description of the uncertainty calculations can be found in Supplement Text S1. The intermediate precision and inlet recovery experiment results were used in the calculation of U by using the 95 % confidence level.</u>

#### 2.3.6 Ozone reactivity tests

- It is well-known that compounds can be lost during sampling due to reactions with ozone. Since some terpenoidsterpenes are highly reactive towards ozone and the ozone reaction rate coefficients ( $k_{03}$ ) of diterpenes are uncertain (Haberstroh et al., 2018;Yáñez-Serrano et al., 2018;Yee et al., 2018), experiments focusing on analyte stability upon ozone exposure were conducted. The sorbent tube was loaded with known amount of analytes (c=40–200 ng) and the tube was flushed with either 0 ppb or 40 ppb of ozone during different times (from 0 to 240 min at 100 mL min<sup>-1</sup> flow rate). The total purge volume of the
- 230 sorbent tube was 0–24 L. The ozone concentration of 40 ppb was selected since it represents a typical upper concentration level in background air in southern Finland (Anttila and Tuovinen, 2010). Ozone was produced by using an ozone generator (model 49C O<sub>3</sub> Calibrator, Thermo Environmental Instruments Inc., Franklin, MA, USA). The schematic illustration of the setup is presented in Fig. S3.

#### 2.4 Applications to real samples

- 235 Two types of real sample applications were selected in order to test the analytical method performance, to identify compounds emitted by boreal forest tree species and to quantify the emissions from a branch enclosure. The first sample application was a dynamic headspace sampling of compounds emitted by needles/twigs in a closed chamber upon heating, and the second sample application was a study of emissions from a branch enclosure in field conditions. The main emphasis on real sample applications was set on the identification and study of DTs, although MTs and SQTs were also monitored. Based on previous
- 240 studies, it was considered that since the DTs seem to be emitted from plant storage pools and since temperature has been shown to be a driving force for DTs emissions (Haberstroh et al., 2018;Matsunaga et al., 2012;Yáñez-Serrano et al., 2018), heating of the plant materials would be an efficient way for releasing the DTs into gas-phase. Thus, the studied plant material samples were firstly heated to temperatures ranging from 30 °C to up to 70 °C in order to obtain presumably detectable amounts of DTs to allow their identification and quantification.
- 245 Pine (*Pinus sylvestris*) needles and, spruce (*Picea abies*) twigs and birch (*Betula pubescens* and *Betula pendula* mixed) leaves were collected during early September 2018 in a boreal forest at the SMEAR II station (Station for Measuring Forest Ecosystem-Atmosphere Relations) in Hyytälä, Finland (Hari and Kulmala, 2005). These plant material samples were

qualitatively and semi-quantitatively analysed for diterpene content. The samples were stored in the dark at -18 °C in a refrigerator for a maximum of 2 months prior to analysis. In a set of experiments, approximately 5–7 g of frozen pine needles

- 250 or small pieced spruce twigs were placed inside a screw-capped 500 mL Duran bottle. The bottle was equilibrated at room temperature for 30 min prior to starting headspace purge-and-trap extraction experiments. The flow in and out of the chamber were set to 200 mL min<sup>-1</sup> and 100 mL min<sup>-1</sup>, respectively. During the dynamic sampling, the bottle was placed inside an oven and heated in 5–10 °C steps from room temperature to up to 70 °C. The sorbent tube samples were collected outside the oven at room temperature for 20 min (sampling volume 2 L). The schematic illustration of the setup is presented in Fig. S4. The dry
- 255 weight of the sample needles were 1.66–2.70 g (drying at 70 °C for 24–48 h). These samples were analysed with emphasis solely on the identification of DTs. <u>Blank samples (empty chamber heated) were collected prior to experiments.</u> Branch enclosure emissions were studied on-site at the SMEAR II station as a proof-of-concept type of experiment on two different days\_(i.e. to test and to demonstrate that the analytical procedure is suitable for the purpose it was intended for). Spruce (*Picea abies*) branch with needles was placed inside a ca. 1.2 L Teflon bag cuvette (same as in Sect. 2.3.3, but shrank).
- 260 which was connected to a fixed plate with inlet and outlet ports. The incoming air (at flow rate of 8.2 L min<sup>-1</sup>) was purified with a high capacity gas purifier (Supelco, Bellefonte, PA, USA) and passed through a ca. 1 m long copper tube (o.d. 12 mm) wrapped with a heating wire and insulator cover (copper tubing was used for improving heat transfer). The incoming air was heated to increase the cuvette inside temperature in order to artificially promote the BVOCs emissions of DTs. A data logger with temperature sensor was placed-used for monitoring inside the cuvette inside temperature. The cuvette was additionally
- 265 covered with aluminium foil for further insulation in order to achieve sufficiently high temperatures. The cuvette inside temperature ranged from 14 to 61 °C and the heating gradients are presented in Fig. S5. Sorbent tube samples were collected either directly from the outlet port of the cuvette or from a bypass flow (outlet flow rate 1.0 L min<sup>-1</sup>). The schematic illustration of the setup is presented in Fig. S6. The branch enclosure experiment sampling dates were 6<sup>th</sup> and 10<sup>th</sup> of August, 2019. On the former date, the samples were collected from a bypass flow and on the latter day directly from the cuvette outlet port. The
- 270 branch was cut immediately after the sampling was completed, thus, it is plausible that the tree was under stress on the latter day experiments. The dry weight of the needles were 6.35–6.75 g (drying at 70 °C for 24–48 h). <u>Blank samples (empty cuvette</u> heated) were collected prior to experiment.

#### 2.5 Chromatographic data analysis

The <u>unknown-non-target</u> compounds in real sample applications were <u>tentatively</u> identified based on both retention index (RI) values and mass spectra comparison to NIST mass spectral library and/or Adams (2007) library. The n-alkane based RI values were calculated based on both Kovats Index (KI) and Arithmetic Index (AI) as shown in Adams (2007). If an unknown compound could not be <u>tentatively</u> identified <u>with sufficient confidence</u> (either too high RI difference or not adequately matching mass spectra), a proposed compound formula was deduced <u>based on the mass spectra</u> is <u>presented as</u> <u>supplementary information</u>. The non-target compounds that were either tentatively identified or assigned with a formula were then categorised as MTs, SOT and DTs when applicable, the others were categorised as BVOCs. For example, if the non-

9

target compound had the characteristic m/z 272, 257, 243 and 229 ions of DTs and the RI value was representative of DTs (Adams, 2007), the compound was assigned in this study to the plausible DT category. Similar identification procedure of non-target compounds has been used also in previous BVOC studies (e.g. Chan et al., 2016; Hellén et al., 2018; Kännaste et al., 2013; Yee et al., 2018). However, it should be mentioned that even the compounds marked here as *identified compounds* 

285 cannot be declared to be truly accurate The compounds were marked here as *tentatively identified* since the authentic standards were not <u>available analysed</u>, <u>-and</u>-thus the final verification is lacking. <u>The analysed blank samples were used to exclude possible contaminant peaks</u>.

<u>The Nonnon</u>-target compounds <u>detected in real samples</u> were quantified by using a compound from the standard <u>compounds</u> <u>analytes</u> list ( $\alpha$ -pinene, limonene or linalool were used for MTs <u>and for close eluting BVOCs</u>,  $\beta$ -caryophyllene or caryophyllene

- 290 oxide for SQTs and for close eluting BVOCs, and cembrene or ent-kaurene were used for DTs and close eluting BVOCs). Since the non-target compounds were quantified in this manner, the mass concentration results are are merely semi-quantitative. A signal-to-noise (S/N) ratio of 10 criteria was used in non-target compound quantification.
  -Similar quantification procedure for non-target compounds has been used also in previous BVOC studies (e.g. Bouvier-Brown et al., 2009; Haberstroh et al., 2018; Hellén et al., 2018). A signal to noise (S/N) ratio of 10 criteria was used in non-target
- 295 compound quantification.

Emission rate (E) was calculated by using Eq. (2):

$$E = \frac{(C_{out} - C_{in}) \times F}{m}$$

(2)

-equation E=((C<sub>out</sub> - C<sub>in</sub>)\*F)/m, where C<sub>out</sub> is the concentration in the outlet flow, C<sub>in</sub> is the concentration in the inlet flow, F is the flow rate into the cuvette and m is the dry weight of the needles (Ortega and Helmig, 2008). In both real sample applications,
 300 the C<sub>in+</sub> was negligible (or <LOQ) for all compounds, and was subsequently set to zero in the calculations.\_—No blank subtraction was needed in the calculations since most analytes were absent in blank samples.</li>

#### **3 Results and discussions**

The first part of this section covers the TD-GC-MS performance evaluation experiments, and in the latter part the qualitative and semi-quantitative results from the real sample applications are presented.

#### 305 3.1 Method performance results

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#### **3.1.1 Desorption and chromatographic separation**

One of the very first experiments performed were the desorption efficiency tests and evaluation of the chromatographic separation of the MTs, SQTs and DTs. The desorption efficiency was  $\geq$ 99.8 % for all compounds with the TD-GC-MS1 at 300 °C for 5 min. With the TD-GC-MS2<sub>7</sub> desorption time needed to be increased from 1 min to 5 min at 300 °C (both sorbent and cold trap) to minimise the carryover, which arise either from the sorbent tube or cold trap, and to obtain sufficient

desorption efficiency (>99.7%). Higher desorption temperatures were not tested to avoid sorbent deterioration in long-term use.

The chromatogram from a standard solution analysis with TD-GC-MS1 is shown in Fig. 1, and more detailed versions are shown in Figs. S7-8 for both TD-GC-MS instruments. The separation was considered to be adequate since all compounds

315 could be baseline separated. The RI values for each compound are presented in Table 1 (according to run with TD-GC-MS1).

#### 3.1.2 Compound stability in storage

The stability was acceptable (>80 %) with most of the compounds still after the 2 months storage period (Fig. S9). On average, MTs were recovered at  $101\pm2$  %,  $93\pm5$  % and  $97\pm4$  % after 5 days, 1 month and 2 month storage, respectively. Similarly, SQTs were recovered on average at  $104\pm2$  %,  $89\pm3$  % and  $94\pm5$  % after 5 days, 1 month and 2 month storage, respectively. Of the diterpenes, ent-kaurene and 3-MA were recovered even after the 2 months storage within acceptable limits (roughly  $80\pm25$  %, Fig. S9), however, cembrene had been lost to  $49\pm18$  % already after 1 month storage. It is unknown why cembrene

seem to have decomposed during the first month of storage, yet then stayed relatively stable until the next month (Fig. S9, from  $49\pm18$  % to  $52\pm33$  %). No decomposition product of cembrene could be identified in the chromatograms.

#### **3.1.3 Recovery results**

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- In Fig. 2a are shown the amount of each compound detected in the first sorbent tube (after the mixing line, Fig. S1a) and the expected theoretical amount calculated based on the experimental conditions used. As can be seen in Fig. 2a, tThe observed amounts were mostly in close agreement with the expected amounts. and although Although this was not a prerequisite for the recovery experiments, the relative recovery was calculated based on amounts found in tubes before and after the sampling line, it demonstrates that the experimental setup was working adequately in practice (although the reproducibility was a bit poor with for some compounds, see Fig. 2a). The injection t-piece needed to be heated to 60 °C in order to increase the volatilisation of the diterpenes. If there was no heating applied, then e.g. ent-kaurene yield in the first tube was less than 20 % of the expected amount (data not shown). The diterpenes were observed to stick into the walls of the injection PTFE t-piece if
- it was not heated, thus heating is recommended to be used in similar experiments. <u>Higher temperatures were not tested here in</u> order to avoid the possible PTFE contamination peaks.
- In Fig. 2b are shown the inlet recovery results for both Teflon FEP and ozone removal inlet lines. The recovery results were in acceptable level (100±20 %) for most of the compounds with both inlets. Interestingly, even though heating was required for volatilisation at the injection point, DTs passed the sampling lines completely in gas-phase as demonstrated by the acceptable recoveries. This could have been expected in the case of the heated stainless-steel line (which certainly maintains the compounds in gas\_-phase), but especially the recoveries obtained with the 15 m long Teflon line were very promising in view of real applications. The results indicate that <u>under the applied conditions the</u> Teflon FEP sampling lines do not need to be heated excessively above room temperature (22±1 °C). which simplifies the measurements in field conditions.

In Figs. 2c-2d are shown the recovery values obtained with both inlets at the different RH levels tested. The RH did not affect the recovery levels dramatically with either inlet tested. Only 3-MA had a slightly worse recovery ( $78\pm12$  %) when Teflon inlet was used at low RH level, but acceptable when the RH was high (recovery  $89\pm6$  %). The standard deviation was fairly

345 large for some of the least volatile compounds (ent-kaurene, cembrene, 3-MA and caryophyllene oxide) and occasionally for  $\beta$ -farnesene and terpinolene, which might be due to a combination of the compound properties and experimental variation.

The cuvette recovery results showed some variability (Fig. <u>\$103</u>). As mentioned in Sect. 2.3.3, three different flow rates were tested (inlet flows 6.7, 2.0 and 1.0 L min<sup>-1</sup>). The recovery values were acceptable at all flow rates tested for all other compounds except for the diterpenes (Fig. <u>\$103</u>). For example, tThe recoveries of MTs and SQTs were on average 95±1 % and 94±2 % at 1.0 L min<sup>-1</sup> and 96±1 % and 93±3 % at 6.7 L min<sup>-1</sup> flow rates, respectively. <u>However, t</u>The recoveries of DTs were on average 44±11 %, 80±6 % and 76±4 % at flow rates of 1.0, 2.0 and 6.7 L min<sup>-1</sup>. The poor <u>DTs</u>-recoveries <u>of DTs</u> observed at the lowest flow rate tested indicate that the residence time inside the cuvette was <u>likely</u> too long for these low volatility compounds (note that for MTs and SQTs the recoveries were acceptable). <u>Nonetheless, tThe DT</u> recoveries were seemingly

355 sampling. However, with the highest flow rate tested, the absolute mass concentrations of DTs were very close to LOQ values (Fig. <u>\$103</u>). This was <u>likely</u> related to an experimental problem in the analyte volatilisation setup. The injection t-piece heating was not efficient enough for allowing complete volatilisation of the DTs, since the high flow rate rapidly cooled the t-piece. Therefore, these DT cuvette recoveries need to be considered as tentative results, since the concentrations levels was-were not systematic between the different flow rates tested (Fig. 3). A better sample introduction system would be needed to get the

adequate with the other flow rates tested, indicating that the set flow rate range of ca. 2–7 L min<sup>-1</sup> would beis suitable for

360 volatilisation more systematic at all flow rates under investigation.
<u>Since the RH was shown to have an effect on the recoveries both in the inlet lines and in the branch cuvette, humidity monitoring of the sampling air is recommended.</u>

#### 3.1.4 Validation of the method Analytical figures of merit of the developed TD-GC-MS method

The analytical method validation figures of meritresults are shown in Table 1. The within-day repeatability (n=6) was fairly 365 good for all compounds (relative standard deviation, RSD<5 %), except for caryophyllene oxide which had a fairly high variation ( $\approx$ 19 %). The intermediate precision (n=22 during 4.5 months period) was acceptable for all compounds (RSD<10 %), when calculated based on the quantified mass concentrations in the sorbent tube (Table 1). The expanded measurement uncertainty (U) at 95 % confidence level for terpenes varied between 1716-40-27 % and between 17-55% with the ambient air sampling and branch enclosure emission procedures, respectively. which was considered to be fit for purpose.

370 In general, the LOQ values (expressed as absolute amount in sorbent tube) were the lowest for monoterpenoidsterpenes (13– 88 pg) and for sesquiterpenes (33–198 pg), and the highest for caryophyllene oxide (340 pg) and diterpenes (287–518 pg). The highest LOQ values were observed in the case of DTs likely because the baseline was the noisiest at the end of the chromatogram and because these compounds had minor contaminant peaks in some of the blank sorbent tubes. When converted to pptv units by assuming-using a sampling volume of 5 L, the LOQ values were approximately 0.5–2.8 pptv for MTs, 0.8–

- 375 7.5 pptv for SQTs and 5.1–9.3 pptv for DTs. These are on a similar level as the method detection limits reported for MTs and SQTs in previous GC-MS studies (Bouvier-Brown et al., 2009;Hellén et al., 2018;Jones et al., 2014;Mermet et al., 2019;Sheu et al., 2018), e.g. Pankow et al. (2012) reported detection limits (S/N-ratio of 10) of 0.7–2.1 pptv for MTs and 0.9–1.4 pptv for SQTs. In addition, the LOQ values obtained in this study by TD-GC-MS were much better than the detection limits recently reported by proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS), which were approximately 90 pptv for
- 380 MTs, 200 pptv for SQTs and 510 pptv for DTs (Yáñez-Serrano et al., 2018).

The calibration curve ranges were approximately 0.2–55.8 ng for MTs, 0.2–61.2 ng for SQTs and 0.4–200.0 ng for DTs. A fairly high concentration range was used in order to cover both the low (atmospheric air) and high (enclosure emissions) concentration applications with a single method. A quadratic fit and intercept set to zero was used in calibration for all compounds. The regression fit of the calibration curves was evaluated based on residual analysis. The calibration curve correlation coefficient was typically  $\geq 0.998$  for all compounds.

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#### 3.1.5 Online vs. offline sampling with TD-GC-MS1

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A detailed version of the results from the comparison between offline and online mode sampling with TD-GC-MS1 is presented in the Text S24 (Figs.  $\frac{S11S10}{S17S16}$ ). Here, a short summary of the observations is presented. In online sampling mode, samples are collected through the TD unit sampling lines, valves and an empty sorbent tube directly onto the cold trap (Fig. <u>S11S10</u>).

Collectively, the results indicated that some of the analytes are lost in excessive amounts in the online sampling mode. For example, when the material of the empty tube used in online sampling was stainless-steel, the concentrations of  $\beta$ -farnesene, caryophyllene oxide and DTs were below LOQ in online mode results. Yet, the recoveries (conline/coffline\*100%) of MTs and other sesquiterpenes were acceptable, on average  $96\pm6$  % and  $84\pm10$  %, respectively. Interestingly, a substantial portion of the 395 compound losses could be explained by the losses onto the empty tube used in online sampling, e.g. the amount of  $\beta$ -farnesene lost in the empty tube was ca. 44%. However, simultaneously a substantial portion of the losses could not be explained by losses onto the empty tube, e.g. up to 98% of the ent-kaurene losses could not be accounted for. Interestingly, about 2 96 % of the compound losses could be explained by losses onto the empty tube used in online sampling, but simultaneously about 4 100 % of the losses could not be accounted for. Somewhat similar observations have been made in previous studies, e.g.

400 Arnts (2010) observed significant SQT losses on stainless-steel tube (about 60 % was missing) and Helmig et al. (2003) found that high sampling system temperatures (110–170 °C) were needed to prevent SOT losses in their setup. Heating to such high temperatures was not feasible in our setup and was not tested.

The online mode sampling efficiency of  $\beta$ -farnesene, caryophyllene oxide and DTs could be increased by changing the empty tube material from stainless-steel to glass and by adjusting the sample air relative humidity (Fig. 34). Increasing the sample air

405 RH improved the recoveries of the aforementioned compounds no matter the tube material, however, the absolute recoveries were otherwise better with the glass tube than with the stainless-steel tube. Most notably,  $\beta$ -farnesene results were consistent and the recovery was good (92±5 %) when the glass tube was used in online mode. Caryophyllene oxide and diterpenes could be detected, but recoveries were fairly poor and had a high uncertainty.

In summary, the online sampling results were in close agreement with the offline sampling results for most of the analytes, 410 demonstrating the online TD-GC-MS method applicability for the quantitative analysis of MTs and SQTs. However, a large discrepancy and poor repeatability was observed between online and offline mode sampling results in the case of diterpenes and caryophyllene oxide. By using glass tube (or glass coated stainless-steel tube, Text S2+) and humidified air the recoveries improved, but further development (e.g. heating of the all lines, valves and sorbent tube in the TD) would be needed for quantitative analysis of diterpenes and caryophyllene oxide. Since the RH was shown to have an effect on the recoveries. 415 humidity monitoring of the sample air stream is recommended

#### 3.1.6 Ozone exposure and losses of terpenoidsterpenes

As explained in Sect. 2.3.6, sorbent tubes containing the analytes were purged with either 0 ppb or 40 ppb of ozone from 0 to 24 L of total purge volume. In theory, the absolute amount of a compound should stay constant in the sorbent tube if the compound is not reacting with ozone or if breakthrough volume is not reached. The zero experiments ( $O_3=0$  ppb) were used

- 420 as a reference to estimate the possible breakthrough, although it was not expected that the terpenoidsterpenes amounts would decrease dramatically due to breakthrough (Sheu et al., 2018). The ozone exposure experiments ( $O_3=40$  ppb) were done in order to estimate the possible losses caused by ozone, and the results were also applied to estimate ozone reaction rate coefficients ( $k_{O3}$ ) for the analyte diterpenes. The results for all compounds are shown in the Fig. S18 and few selected plots are presented in Fig. 4<u>5</u>.
- 425 Based on the  $O_3=0$  ppb purging results, breakthrough volume (50 % lost, BTV<sub>50%</sub>) was not reached with any of the compounds under the applied experimental conditions (Fig. <u>S18S17</u>). At the highest purge volume of 24 L, the relative amount of all compounds were higher than 0.87 and on average 0.97±0.05 for MTs, 0.96±0.05 for SQTs and 0.98±0.02 for DTs. Thus, any decrease observed in the following  $O_3=40$  ppb results was attributed to be due to ozone reaction losses.
- The O<sub>3</sub>=40 ppb purging results seemed reasonable for most of the compounds when considering the compound specific  $k_{O3}$ values (Fig. <u>S18-S17</u> and Table S3). In general, the linear regression fit (relative amount in sorbent as a function of purge volume) slopes were declining the fastest with compounds that had the largest  $k_{O3}$  values (i.e. compounds which react the fastest with ozone are subsequently lost rapidly from the sorbent tube). However, this trend analysis also revealed that the literature reported predicted diterpenes  $k_{O3}$  values might be slightly misleading (Haberstroh et al., 2018). For example, as can be seen in Fig. <u>4-5</u> upper panel plots, the slope declined the fastest as the  $k_{O3}$  increased in the order of camphene, limonene and
- 435  $\beta$ -caryophyllene, however, ent-kaurene  $k_{03}$  value is somewhat lower than would be expected based on the slope decline. In the lower panel plot of Fig. 45, literature retrieved ln ( $k_{03}$ ) values were plotted as a function of the slopes obtained from the ozone purging experiments (Table S3 and Fig. S18), similar as done in Pollmann et al. (2005). As can be seen in Fig. 4-5 and Table S3, the predicted literature  $k_{03}$  value of cembrene is in close agreement with the obtained experimental value, whereas the corresponding ent-kaurene  $k_{03}$  value would be actually 2 orders of magnitude higher based on the linear regression fit.

440 Based on this simple estimation process, the ozone reaction rate coefficients for ent-kaurene and cembrene were  $(1.4\pm8.2)x10^{-1}$  $^{15}$  and  $(2.4\pm15.5)\times10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. Consequently, the estimated lifetimes of DTs were on average 11±4 min, whereas the estimated lifetimes of MTs and SQTs were in the range of 6-4800 min and 5-3800 min, respectively (calculated by assuming atmospheric concentration of  $O_3=40$  ppb).

These ozone exposure results indicate that ozone removal should be used prior to sampling of terpenoidsterpenes. Several

445 different kind of ozone traps and filters have been used to trap ozone, but some of them are not suitable even for monoMTsand sesquiterpenesSOTs (Pollmann et al. 2005, Calogirou et al. 1996). In addition, some of the ozone removal techniques have very short ozone removal capacity and they have to be changed frequently and are therefore not ideal for online sampling (Bouvier-Brown et al. 2009, Fick et al., 2001). Based on the ozone removal results presented in Hellén et al. (2012) and the inlet recovery results presented in this study (Fig. 2d), heated stainless-steel line could be an optimal good solution for ozone removal especially in online sampling. 450

#### **3.2 Real sample application results**

Prior to the dynamic headspace extraction of real samples outlined in Sect. 2.4, preliminary solvent extraction of needles, twigs and leaves were conducted by using ultrasonication assisted extraction with methanol and dichloromethane. The tentative qualitative screening of these solvent extracts indicated that there were no DTs present in the birch leaves, whereas in pine 455 needles and spruce twigs, diterpenes could be detected (data not shown). Similarly, Kanerva et al. (2008) did not observe any diterpenes in their essential oil analysis of silver birch leaves, but found diterpenes in Scots pine and Norway spruce needles. Therefore, birch leaves were not further studied in the following experiments. As explained in Section 2.4., in the following experiments the plant material samples were heated in order to characterize the DTs potentially emitted by the studied tree species and to further test the TD-GC-MS method performance in view of real sample analysis. The plant material samples 460 were heated to facilitate the release of DTs from the plant storage pools into the gas-phase.

3.2.1 Headspace extraction of heated pine needles and spruce twigs

From the dynamic headspace sampling of heated pine needles and spruce twigs several diterpenes could be detected, however, these compounds were detected mainly at the highest temperatures tested and eventually in quite low concentrations. The chromatograms of pine needles and spruce twigs samples are shown in Figs. S19 S206 and 7 and the detected peaks are outlined in Table S4.

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In total, 11 hydrocarbon diterpenes ( $C_{20}H_{32}$ ), two oxygenated diterpenes ( $C_{20}H_{34}$ ) and one unidentified-unknown BVOC  $\frac{\text{compound}(C_{19,20}H_{28,30})}{\text{Fig. 7 and Table S4}}$  of the headspace samples of spruce twigs (Fig. 7 and Table S4). Of these 14 compounds, only five could be positively tentatively identified based on mass spectra and retention index matches (Fig. S20 and Table S4). The identified compounds were rimuene, cembrene, cembrene A, 13-epi-manool oxide and abietatriene. Most of these

470 compounds have been detected previously in spruce essential oil samples (Norin and Winell, 1972; Wajs et al., 2006), with the exception of rimuene which, however, has been observed recently in ambient air in Amazon (Yee et al., 2018).

In the pine needles samples, only few DTs could be detected, however, several other similar  $C_{18-20}H_{26-32}O_{0-2}$  type of BVOCs compounds-were observed (Fig. 6 and Table S4). Overall, three hydrocarbon diterpenes, two oxygenated diterpenes and eight other similar high molecular weight compounds (with potential formulas of e.g.  $C_{19}H_{30}$ ,  $C_{18}H_{26}O$  and  $C_{20}H_{28}O$ ) were detected.

475 Of the 13 compounds observed, only three could be tentatively identified. (Fig. S19 and Table S4). These identified compounds were sandaracopimaradiene, 13-epi-manool oxide and abietadiene. Of these DTs, only abietadine has been found also previously in pine essential oil samples (Judzentiene and Kupcinskiene, 2008;Judžentienė et al., 2006;Kupcinskiene et al., 2008: Tumen et al., 2010). Most of those previous studies have detected also manool oxide, which is a stereoisomer of 13epi-manool oxide that we observed here. Interestingly, sandaracopimaradiene has been observed also in the ambient air in

480 Amazon (Yee et al., 2018).

> Unfortunately, some of the peaks that had the same (or *almost* the same) retention index values in spruce and pine samples (Table S4), could not be assigned to be the same compound based on mass spectra. Therefore, it is possibleible that there might be overlapping compounds in the chromatograms. However, since the mass spectra were different, it is equally possible that the overlapping compounds do not affect the quantification since they seemed to be species specific.

- 485 Emission rate coefficients (Fig. <u>\$21</u>\$18-<u>\$22</u>\$19) were calculated in order to evaluate specifically the relative amount of DTs emitted in comparison to MTs and SQTs. These results are merely semi-quantitative and the uncertainties might be fairly high (e.g. all detected diterpenes were quantified based on either ent-kaurene or cembrene, and some MTs had higher concentrations in samples than in standards, so the calibration needed to be extrapolated for obtaining mass concentrations). Only the standard analyte MTs and SQTs found in samples were quantified-(i.e. non-target MTs and SQTs are not accounted for). The results 490 from spruce twigs at 70 °C are not presented due to moisture related problems in the experiments.
- As can be seen in Fig. 58, the emission rates were generally roughly 1 to 3 orders of magnitude lower for DTs when compared to MTs and SQTs (see also Figs. S21S18-22-19 for individual compound plots). In general, the emission rates increased as the temperature increased with all compounds. At 30 °C, MTs and SQTs emission rates from pine needles were on average  $464\pm431$  and  $50\pm71$  ng g<sub>dw</sub><sup>-1</sup>h<sup>-1</sup>, respectively. At the same conditions, the emission rates of DTs were on average only  $1\pm1$  ng
- 495  $g_{dw}^{-1}h^{-1}$ , and of the five DTs detected in total, only three were above LOQ at 30 °C. Similarly, the emission rates at 30 °C from spruce twigs were 1052 $\pm$ 825 and 164 $\pm$ 97 ng g<sub>dw</sub><sup>-1</sup> h<sup>-1</sup> for MTs and SQTs, respectively. Of the 12 DTs observed in spruce twigs emissions, only one was above LOQ at 30 °C (at emission rate of 1 ng gdw<sup>-1</sup>h<sup>-1</sup>). At 60 °C the emission rates of MTs and SQTs were roughly 2-fold higher than those observed at 30 °C in both pine needles and spruce twigs samples, however, the corresponding increase in the emission rates of DTs were roughly 30- to 85-fold (up to  $70\pm129$  ng  $g_{dw}^{-1}h^{-1}$ ). Clearly the increase in DTs emissions was more drastic than the increase in MTs and SQTs emissions as the temperature increased (Fig. 85).
- 500

#### 3.2.2 Branch enclosure experiments

The branch enclosure experiments of a living tree in a boreal forest were conducted in view of the results obtained in the previous section. Since it was though that the DTs emissions would need drastic conditions (e.g. drought, warm temperatures, direct sunlight, pest stress) to be emitted in detectable amounts, the cuvette was artificially heated to high temperatures to

- 505 promote the DT emissions in order to swiftly test the method in practice. The cuvette inside temperature was heated from ca. 14 to 61 °C in the course of the day (from morning to afternoon, Fig. S5). As mentioned in Sect. 2.4, the sorbent tube sampling was performed either from a bypass flow or directly from the cuvette outlet port on two different sampling dates. These experiments were conducted in a proof-of-concept type of approach. <u>TD-GC-MS2 was used for analysis since the TD-GC-MS1 was not available at the time of these experiments.</u>-
- A full list of compounds detected in the spruce emissions are shown in Table S5 and an example chromatogram from a sample analysis in Fig. <u>\$23\$20</u>. In total, <u>19-25</u> MTs, 14 SQTs, <u>seven-six</u> DTs and <u>15-10</u> other <u>B</u>VOCs were detected (Table S5). The DTs were mainly detected once the enclosure temperature was higher than 40 °C and most DTs were detected only at ca. 60 °C. Most of the here <u>tentatively</u> identified compounds have been observed previously in essential oil samples, headspace samples or branch enclosure emissions from spruce (Hakola et al., 2017;Kännaste et al., 2013;Radulescu et al., 2011;Wajs et
- 515 al., 2006). Of the seven DTs detected, three could be positively identified. Similar to the results of spruce twigs in Sect. 3.2.1, the DTs rimuene and cembrene were identified in these branch enclosure experiments. However, the other DTs and alike compounds could not be verified to be matching between the different spruce sample types. This lack of similarity might be simply due to chemotypic variability between the trees (Bäck et al., 2012;Hakola et al., 2017). The one tentatively identified DT was assigned to be 13-epi-manool, although it might be as well manool (the difference in RI and mass spectra is not that
- 520 evident between these two stereoisomers), which has been detected previously in spruce samples (Kanerva et al., 2008;Radulescu et al., 2011).

Similar as in the previous section, DTs emission rates were calculated for the relative comparison to MTs and SQTs values. These emission rate results are merely semi-quantitative and have high uncertainty (e.g. some MT concentrations were above the calibration range), thus the results should be evaluated with caution. The emission rates were quite different on the two

- sampling dates tested (Fig. <u>96</u>). On the first sampling date, the MTs, SQTs and DTs emission rates were on average <u>45454784±60275845</u>, 321±247 and 67±87 ng  $g_{dw}^{-1}h^{-1}$  at 60±1 °C, respectively. On the latter date, the emission rates at 59±1 °C were on average 802<u>48±102289712</u>, 641±308 and 419±197 ng  $g_{dw}^{-1}h^{-1}$  for MTs, SQTs and DTs, respectively. The MTs and SQTs emission rates were roughly 2-fold higher on the latter day, whereas the DT emission rates were then approximately 10 times higher than on the first sampling day. In relative terms, the DT emissions were significantly higher on the latter day,
- 530 for example, the respective DT/SQT-ratio increased from 9 % to 48 % between the sampling dates. It is likely that the difference observed in results between the two sampling dates is due to the stress induced by cutting the branch and the related experimental work on the first sampling date. Nonetheless, in field conditions the difference in DTs emission rates in comparison to MTs and SQTs emission rates were similar as in the laboratory headspace sample (roughly 2- to 70-fold difference on average at ca. 60 °C).

#### 535 4 Conclusions

An analytical method using sorbent tube sampling followed by TD-GC-MS analysis for the determination of monoterpenoidsterpenes (MTs,  $C_{10}$ ), sesquiterpenoidsterpenes (SQTs,  $C_{15}$ ) and diterpenoidsterpenes (DTs,  $C_{20}$ ) in gas-phase samples was developed. The intermediate precision (3–10 %) and expanded measurement uncertainties ( $\frac{1716-40-55}{5}$ %) for terpenoidsterpenes were considered to be adequate and fit-for-purpose. The LOQ values for MTs, SQTs and DTs were 13–88

- pg, 33–340 pg and 287–518 pg, respectively. If <u>using assuming</u> a sample volume of 5 L would be used in offline sampling, then the LOQ values were would be approximately 0.5–2.8 pptv for MTs, 0.8–7.5 pptv for SQTs and 5.1–9.3 pptv for DTs. In general, the method development and performance experiments results were good, especially in view of the DTs results. For example, tThe sampling recovery results (15 m long Teflon FEP line, 1 m heated stainless-steel line and a Teflon cuvette bag) were mostly acceptable (within 100±20 %) for all studied compounds. For example, the recoveries of DTs were on
- 545 average 86±1% and 85±6% when the 1 m heated stainless-steel and 15 m Teflon FEP sampling lines were tested, respectively. These sampling recovery results of DTs were promising, since they demonstrated that the DTs were not lost in excessive amounts in the sampling lines tested. These sampling recovery results indicated that conventional sampling inlet setups can be used as such also with DTs (i.e. no heating of Teflon lines is required).
- Comparison of online mode sampling and offline mode sampling with TD-GC-MS1 revealed that some of the terpenoidsterpenes are lost in excessive amounts in the online sampling mode. The online mode sampling efficiency could be improved by changing stainless-steel surface to glass in the sample path and by increasing the sample air relative humidity. However, based on the tentative experiments, the online mode TD-GC-MS sampling is only valid quantitatively for monoterpenoidsterpenes and some sesquiterpenes. Diterpenes and caryophyllene oxide results were poor in online sampling mode even with the best possible set up tested (recoveries typically <70 %), limiting the applicability only to semi-quantitative
- 555 or qualitative analysis. These online mode recovery results highlight the importance of testing each experimental setup in practise prior to conducting campaign measurements.

Based on the ozone reactivity experiments conducted, the literature reported predicted ozone reaction rate coefficients ( $k_{O3}$ ) of some diterpenes might be underestimated. Our results indicated, that the experimentally derived  $k_{O3}$  value of ent-kaurene was approximately 2 orders of magnitude higher than the literature predicted  $k_{O3}$  value. Consequently, the role of diterpenes in

560 atmospheric oxidation reactions could be more profound than predicted. In addition, the results also highlight the difficulties related to the determination of DTs in ambient air. Theoretically, the emissions of DTs are very low to begin with and the high reactivity decreases the concentrations even further, making the time frame of DT analysis extremely short. Based on the real sample applications results, we could characterise the DTs emitted by Norway spruce and Scots pine-(in-

birch samples DTs could not be detected). Multiple DTs  $(C_{20}H_{32-34}O_{0-1})$  and similar high molecular weight compounds BVOCs

565 ( $C_{18-20}H_{26-32}O_{0-2}$ ) could be detected in the emissions, however, only few could be <u>tentatively positively</u> identified. Of the DTs <u>tentatively</u> identified in this study (e.g. rimuene, cembrene, sandaracopimaradiene, 13-epi-manool oxide and abietadiene), many have been detected previously in essential oil samples and/or even in atmospheric air elsewhere. The DTs emitted by

different tree species were partly species specific (e.g. cembrene and rimuene were observed in spruce emissions, but not in pine emissions). It would be beneficial to perform similar experiments with other tree species for comparability, and in order

570 to identify the possible common/specific DT traces.

In general, the semi-quantitatively estimated DTs emission rates were roughly 1 to 3 orders of magnitude lower than the MTs and SQTs emission rates. Diterpenoidsterpenes were mostly emitted at high temperatures (typically  $\geq$ 35 °C) and the temperature dependence in emissions of DTs was relatively more profound than in those of MTs and SQTs. In principle, the results indicated that high temperatures are needed for instrumentally detectable levels of DTs to be emitted in branch enclosure

575 measurements. These conditions could be met, for example, during direct sunlight exposure and in sunny warm days. In addition, the highest temperatures tested in this study (up to 60 °C) might be reached under extreme situations during atmospheric measurements, such as in the surroundings of forest fires. Long-term measurements in real-life field conditions would be required to truly study the emissions of DTs (in addition to other terpenoidsterpenes and BVOCs) and their atmospheric relevancy.

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Data availability. Data available upon request by contacting the corresponding author (aku.helin@fmi.fi).

*Author contributions*. AH, HaHa and HeHe designed the experiments, and AH and HeHe carried them out. AH and HeHe performed the data analysis. AH prepared the manuscript with contributions from all co-authors.

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Competing interests. The authors declare that they have no conflict of interest.

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Compound	CAS Number	Formula	RIª	Quan _tify m/z ion	LOQ in pg (in pptv) <sup>b</sup>	Repea- tability (RSD %)	Inter- mediate precision (RSD%)	<u>U</u> ° (%)	U <u>d</u> (%)
α-Pinene ( <u>MT)</u>	7785-70-8	$C_{10}H_{16}$	945 (942)	93	34 (1.2)	2.6	3.8	<u>16</u>	<u>18</u> 17
camphene (MT)	79-92-5	$C_{10}H_{16}$	963 (960)	93	14 (0.5)	1.6	4.0	<u>16</u>	<u>18</u> 18
β-pinene ( <u>MT)</u>	19902-08-0	$C_{10}H_{16}$	989 (988)	93	13 (0.5)	4.2	3.2	<u>17</u>	<u>20</u> 18
3-carene (MT)	498-15-7	$C_{10}H_{16}$	1018 (1017)	93	18 (0.6)	2.0	3.3	<u>16</u>	<u>17</u> 17
<i>p</i> -cymene (MT)	99-87-6	$C_{10}H_{14}$	1033 (1031)	119	20 (0.7)	2.0	4.2	<u>17</u>	<u>19</u> 19
Limonenelimonene (MT)	5989-54-8	$C_{10}H_{16}$	1039 (1037)	68	62 (2.2)	1.5	3.8	<u>17</u>	<u>17</u> 17
1,8-cineol ( <u>MT)</u>	470-82-6	$C_{10}H_{18}O$	1044 (1042)	154	27 (0.9)	2.6	4.7	<u>18</u>	<u>20</u> 18
Terpinolene (MT)	586-62-9	$C_{10}H_{16}$	1094 (1093)	121	65 (2.3)	2.5	5.0	<u>17</u>	<u>18</u> 17
Linalool <u>linalool</u> ( <u>MT)</u>	78-70-6	$C_{10}H_{18}O$	1100 (1100)	71	88 (2.8)	2.4	4.8	<u>18</u>	<u>18</u> 18
4-acetyl-1- methylcyclohexene (4- AMCH) <u>(BVOC)</u>	6090-09-1	$C_9H_{14}O$	1140 (1139)	95	120 (4.2)	2.7	6.3	<u>19</u>	<u>20</u> 20
Nopinonenopinone (BVOC)	38651-65-9	$C_9H_{14}O$	1154 (1153)	83	29 (1.0)	2.7	5.3	<u>18</u>	<u>21</u> 48
<u>b</u> Bornylacetate (BVOC)	5655-61-8	C <sub>12</sub> H <sub>20</sub> O 2	1295 (1294)	95	49 (1.2)	2.4	6.2	<u>20</u>	<u>23</u> 20
Longicyclenelongicycl ene (SQT)	1137-12-8	C <sub>15</sub> H <sub>24</sub>	1401 (1401)	94	35 (0.8)	2.4	4.9	<u>18</u>	<u>21</u> <del>19</del>
Isolongifolene <u>isolongif</u> olene (SQT)	1135-66-6	$C_{15}H_{24}$	1422 (1422)	161	38 (0.9)	2.5	5.7	<u>19</u>	<u>22</u> 20
β-caryophyllene	87-44-5	$C_{15}H_{24}$	1445 (1444)	93	105 (2.5)	2.2	3.5	<u>17</u>	<u>22</u> <del>17</del>
β-farnesene (SQT)	18794-84-8	$C_{15}H_{24}$	1457 (1456)	69	198 (4.7)	5.0	5.9	<u>20</u>	<u>22</u> 25
$\alpha$ -humulene (SQT)	6753-98-6	$C_{15}H_{24}$	1481 (1480)	93	33 (0.8)	2.1	4.2	<u>18</u>	<u>24</u> 18

795 Table 1. List of analytes, corresponding retention indices (RI) and analytical figures of merit.

caryophyllene oxide (SQT)	1139-30-6	$C_{15}H_{24}O$	1612 (1612)	79	340 (7.5)	18.9	8.6	<u>24</u>	<u>28</u> 24
Cembrenecembrene (DT)	1898-13-1	$C_{20}H_{32}$	1959 (1959)	93	287 (5.1)	4.0	9.5	<u>27</u>	<u>52</u> 40
ent-kaurene (DT)	562-28-7	$C_{20}H_{32}$	2106 (2106)	257	518 (9.3)	2.9	7.7	<u>26</u>	<u>42</u> 27
3-methylene-5-α- androstane (3-MA) <sup>e</sup> (DT)	not assigned	$C_{20}H_{32}$	2153 (2152)	257	383 (6.9)	3.0	7.2	÷	27

<sup>a</sup> RI as Kovats indices (and arithmetic indices in brackets)

<sup>b</sup> LOQ in pptv calculated by using sample volume of 5 L (at T=298 K and p=1 atm)

<sup>c</sup> U (%) for ambient air application

<sup>d</sup> U (%) for branch enclosure emissions application

800 e The purity of this crude standard was set to being 100% (allowing the determination of LOQ, but unknown uncertainty).



Figure 1. Overlaid selected ion recording (SIR) chromatograms of a standard solution (c=10-50 ng in sorbent tube) analysed by TD-GC-MS1. The analysis conditions are presented in Table S2. Peak identification can be made based on Table 1, from low RI (peak 1.  $\alpha$ -pinene) to high RI (peak 21. 3-MA).



Figure 2. Inlet recovery experiment results: (a) calculated theoretical amount and observed amount in the first sorbent tube (n=18), (b) inlet recovery levels at laboratory room conditions (n=9 with both inlets), (c) inlet recovery levels at different RH levels with Teflon FEP inlet (n=8-10) and (d) with heated stainless-steel inlet (n=9-10). The error bars represent reproducibility (n=8-18).



810 Figure 3. Cuvette recovery results (top panel plot) and the absolute amount detected in the first sampling sorbent tube presented according to the different inlet flow rates used (the lowest three panel plots). The theoretical expected amount was calculated based on the used experimental conditions. The error bars represent reproducibility (*n*=3-9).



Figure <u>43</u>. Comparison of online sampling mode recoveries obtained by using either empty stainless-steel (SS) tube (at RH=5 %) or empty glass tube (at RH=70 %) in online sampling. The empty spaces marked with asterisk indicate <LOQ results in online sampling. The error bars represent repeatability (*n*=2).



Figure 45. Results from ozone exposure experiments. In the upper panel plots are selected examples from the ozone exposure experiments presented as relative amount of compound in sorbent tube as a function of purge volume. The values embedded into the plots are the linear regression fit slopes (±uncertainty) of corresponding conditions (either O3=0 ppb or O3=40 ppb). The compound specific ko3 values are presented in the plots as well. The error bars represent reproducibility (*n*=3). In the lower panel plot is presented the literature retrieved ln (ko3) values (see Table S3) as a function of the linear regression fit slopes.



Figure 6. Selected ion recording (SIR) chromatograms from the TD-GC-MS1 analysis of pine needles and blank dynamic headspace sorbent tube samples (sampling at 60 °C for 20 min at a flow rate of 100 mL/min). The five m/z ions included in the SIR were m/z 93, 229, 257, 272 and 275. The chromatogram is scaled for presentation purposes, peak number 9 is not showed in full height in order to visualize the other peaks more clearly. Peak identification: 1. Unknown (C<sub>19</sub>H<sub>30</sub>, BVOC), 2. Unknown (C<sub>19</sub>H<sub>28</sub>, BVOC), 3. Unknown (C<sub>18</sub>H<sub>26</sub>O, BVOC), 4. Unknown (C<sub>19-20</sub>H<sub>32</sub>O<sub>0-2</sub>, BVOC), 5. Unknown (C<sub>20</sub>H<sub>32</sub>, DT), 6. Sandaracopimaradiene (C<sub>20</sub>H<sub>32</sub>, DT), 830
7. Unknown (C<sub>19-20</sub>H<sub>28</sub>O<sub>0-1</sub>, BVOC), 8. Unknown (C<sub>20</sub>H<sub>30-2</sub>, BVOC), 9. 13-epi-manool oxide (C<sub>20</sub>H<sub>34</sub>O, DT), 10. Unknown (C<sub>19-20</sub>H<sub>28-32</sub>O<sub>0-1</sub>, BVOC), 11. Unknown (C<sub>19-20</sub>H<sub>28</sub>O<sub>0-1</sub>, BVOC), 12. Unknown (C<sub>20</sub>H<sub>34</sub>O, DT) and 13. Abietadiene (C<sub>20</sub>H<sub>32</sub>, DT). See Table S4 for further information on peak identification.



Figure 7. Selected ion recording (SIR) chromatograms from the TD-GC-MS1 analysis of spruce twigs and blank dynamic headspace sorbent tube samples (sampling at 60 °C for 20 min at flow rate of 100 mL/min). The five m/z ions included in the SIR were m/z 93, 229, 257, 272 and 275. The TIC is scaled for presentation purposes, peak number 3 is not showed in full height in order to visualize the other peaks more clearly. Peak identification: 1. Rimuene (C<sub>20</sub>H<sub>32</sub>, DT), 2. Unknown (C<sub>20</sub>H<sub>32</sub>, DT), 3. Cembrene (C<sub>20</sub>H<sub>32</sub>, DT), 4. Cembrene A (C<sub>20</sub>H<sub>32</sub>, DT), 5. Unknown (C<sub>20</sub>H<sub>32</sub>, DT), 6. Unknown (C<sub>20</sub>H<sub>32</sub>, DT), 7. Unknown (C<sub>20</sub>H<sub>32</sub>, DT), 8. 13-epi-manool oxide (C<sub>20</sub>H<sub>34</sub>O, DT), 9. Unknown (C<sub>20</sub>H<sub>32</sub>, DT), 10. Unknown (C<sub>19-20</sub>H<sub>28-30</sub>, BVOC), 11. Unknown (C<sub>20</sub>H<sub>34</sub>O, DT), 12. Unknown (C<sub>20</sub>H<sub>32</sub>, DT), 13. Abietatriene (C<sub>20</sub>H<sub>30</sub>, DT) and 14. Unknown (C<sub>20</sub>H<sub>32</sub>, DT). See Table S4 for further information on peak identification.



845 Figure 85. Terpenoid semi-quantitative emission rates from pine needles and spruce twigs as a function of oven temperature in the dynamic headspace extraction experiments. The average (± standard deviation) emission rates MTs, SQTs and DTs were calculated based on data presented in Figs. S21-S22.



Figure <u>96</u>. Semi-quantitative average (±standard deviation) emission rates of MTs, SQTs and DTs from the living spruce branch enclosure experiments on two different sampling dates. The cuvette inside temperature is shown on the right y-axis (for details see Fig. S5). For details on the <u>terpenoidsterpenes</u> included, see Table S5.