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Impacts of soil moisture on de-novo monoterpene emissions from European beech, Holm oak, Scots pine, and Norway spruce

By C. Wu et al.

Final response of the authors to the referees' remarks.

We thank both reviewers for their helpful comments. Whenever possible we followed their suggestions and we feel that the manuscript is improved now.

Before answering to the remarks in detail we would like to stress again that this paper is intended to provide a data set allowing considering the impacts of soil moisture in the Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther et al., 2006, 2012). We therefore provide data for $\Delta\Theta_1$*. Data for* Θ_W *can be obtained from data of Chen and Dudhia (2001) for regional or global scales. Our data on* $\Delta\Theta_1$ *are new and we believe to have achieved our goal to provide parameterization for a realistic modelling of the soil moisture dependence with MEGAN which is the most used model with respect to natural VOC emissions. Changing the reference from* Θ *(volumetric water content related to soil volume) to RWC (relative water content based on water only) would be counterproductive and limit the applicability of our work. For this reason we decided to keep* Θ *as reference quantity. In order to facilitate the use of our data also for other models, we give a number to convert from* Θ *to RWC (end of the new Section 2.5).*

The following text is organised in the following manner: The referees' comments are written in **bold** *and our responses to the remarks are written in italic (font Arial). Changes in the text of the manuscript and cited here are written in font* Times New Roman.

Detailed response to the remarks of anonymous referee #1

Anonymous Referee #1

This paper investigates the effect of soil moisture (SM) on de novo monoterpene (MT) emission of seedlings of 4 tree species. The paper is generally clearly written; the ideas are logically introduced and discussed. The methodology is sound, at least in what concerns MT measurements, because the experimental design and the application and evaluation of drought are less rigorous. The main merit of the paper is the valuable attempt toward modelling the effect of soil water availability on MT emission of 4 widespread tree species. The main flaws are:

1) the election of soil moisture as a reference parameter of soil water availability,
Our response: The aim of our study was to specifically provide new parameters to be adopted in MEGAN for a more realistic prediction of VOC emission in response to soil water content. MEGAN uses the volumetric water content of the soil as reference and our choice of also using the volumetric water content is motivated by this modelling requirement. Using Θ *as reference parameter is thus consequent, on purpose, and not a flaw.*
To make our aim clearer we added the words: "with MEGAN" at the end of the introduction when describing our main aim.

2) the uncertainty authors acknowledge in the measurement of SM (which precludes differentiating the sensibility of MT emission to SM among species),

Our response: This seems to be a misunderstanding. The errors in soil moisture determination are not high. The error margins are normal for such measurements and are thus acceptable. We will respond to this remark in detail when this remark is repeated below.

and 3), the confusing writing of an important aspect as is the validity of a factorial approach to model the effect of several abiotic factors on MT emission.
Our response: Again, these seem to be misunderstandings and we respond to this remark when it is repeated below.

I understand using plants cultivated in pots is almost inevitable to study abiotic factors in controlled experiments. Although I initially saw the use of potted plants as a flaw, there are two questions that made me change my mind: the large volume of pots to grow 2 year-old seedlings and the similar response of MT emission to soil moisture in two experiments with different rate of soil desiccation.

1) I don't share authors' opinion that SM is the best parameter to study and model plant responses to drought; I think soil water potential or relative water content (RWC) are better indicators. For example, RWC is useful for meta-analyses and comparison among experiments because it is independent on the nature of the soil.
Our response: As already mentioned above, aim of our study is to provide data that can be used for modelling and we use the same reference quantity as that used in the well accepted MEGAN model. However, we also understand the referees' request for using our data for other models that operate with RWC. We therefore give a conversion factor (Section 2.5).

2) Authors cannot reliably estimate soil moisture (see P 12993 Line 5 and P 12996 Line 23; 15% error is very high relative to the range of soil moisture they monitor 0-40%), and yet soil moisture has a central role in this paper. On the other hand, authors leave it clear throughout the text, so that readers can decide whether these summed errors in estimating SM invalidate their conclusions or not.
Our response: This seems to be a misunderstanding; the error margins are relative to the absolute values of Θ with Θ_1 as reference point. The error in our determinations of soil moisture is therefore not high. Obviously this point was not clear enough although we pointed out that "The error caused by this procedure for Θ is estimated to be ±15% <u>of the absolute data</u>" (P.12996, lines 22-23) which is a usual idiom.

We obviously underestimated the capability of this idiom to be misunderstood. Giving relative errors in units of % may indeed be misleading for readers familiar with RWC which is often expressed in units of % (please also note that $\Theta = 0.4\ m^3 \cdot m^{-3}$ is not RWC = 40%). To avoid such misunderstanding we now give absolute errors for Θ. We describe the error sources and error limits more explicitly and highlight that the main error basically causes a shift of Θ. The main parameter necessary for modelling with MEGAN, $\Delta\Theta_1$, is only minimally affected. The amended text is written in the new Section 2.5. The new text passage with respect to the uncertainty limits of Θ now reads:

Experimental errors in the determination of Θ were due to the noise on M_{act}, due to the uncertainties of M_{dry} and due to the error in the determination of V_{soil}. The error in volume determination was negligible and, compared to the error in M_{dry}, the error by the noise was of minor importance. The statistical noise of 20 – 30 g (peak to peak noise, deviation from average at maximum ± 15 g) added an uncertainty of ± 15 mL to the volume of water, which is low compared to the total amount of added water (5 – 6 L). At soil volumes of about 13 L, the uncertainty produced by the noise on Θ was ± 0.0012 $m^3 \cdot m^{-3}$.

The error due to our procedure of taking soil samples was higher. Taking samples from the same pot caused differences in the dry mass. Extrapolated to the total mass of the soil the maximum deviation was 420 g leading to an uncertainty of ± 210 g for M_{dry}. This is more than an order of magnitude higher than the uncertainty added by the noise on M_{act}. The uncertainty we give for Θ is therefore mainly based on the uncertainty of M_{dry} which, converted to the water volume is ± 210 mL. The possible error added to Θ by the uncertainty of M_{dry} is: ± 0.016 m^3 m^{-3}.

It has to be noted that the error caused by the different error sources have different qualities: while errors due to the noise are statistical errors, the error caused by uncertainty of M_{dry} is a systematic error for each individual experiment. Errors in M_{dry} mainly cause a systematic shift of the Θ axis. Errors in the zero point may therefore be high and in one case, the measured M_{act} was lower than M_{dry}. This led to slightly negative values for Θ which is physically impossible. However, since the deviation from zero was quite low, we left the negative values.

Erroneous determination of M_{dry} does not impose important uncertainties on $\Delta\Theta_1$. Due to the systematic nature of this error, its main effect is a systematic shift of the Θ axis. As $\Delta\Theta_1$ is the difference between Θ_1 and Θ_0, systematic shifts in Θ cancel out. Hence, total uncertainties in $\Delta\Theta_1$ which is the main parameter for modelling with MEGAN were quite low and thus acceptable.

Besides uncertainties of Θ caused by errors in the determination of M_{act} and M_{dry} there is also an uncertainty due to our fitting procedure. Also MT emissions contain uncertainties and hence, data obtained from fits using the MT emissions as base conserve these uncertainties. Nevertheless, the statements we give on the soil moisture dependence of MT emissions as well as on the differences observed between MT emissions on the one hand and net photosynthesis and transpiration on the other hand are not substantially affected by the errors in Θ.

We hope that the new description of error sources and error margins clarify the misunderstanding and show that all the statements we give in the manuscript on the Θ-dependencies of MT emissions, of net photosynthesis, and of transpiration are justified.

We also added the conversion from Θ to RWC to the new Section 2.5. The text now reads:

To allow using our data also for models that use the relative water content of the soil as reference we give a conversion factor from Θ to RWC. According to Rambal et al. (2003), RWC is the ratio of current water content to water content at field capacity. Using our mass based data, RWC can be calculated according to Eq. (6):

$$RWC = \frac{M_{act} - M_{dry}}{M_{FC} - M_{dry}} \qquad (6)$$

In Eq. (6), M_{FC} is the mass of the soil at field capacity, M_{act} is the actual mass and M_{dry} the dry mass as in Eq. (5). Field capacity is reached when the micropores of the soil are filled with water and the macropores filled with air after water is lost by gravity. According to our procedure of waiting some hours before measuring the weight of pot and plant, the water in the macropores should have been lost. We therefore approximate M_{FC} from the weight shortly after removing the excess water from the dishes below the pots and after subtracting the mass of the empty pot. Setting $RWC = x \cdot \theta$ it follows:

$$x = \frac{V}{M_{FC} - M_{dry}} \cdot \rho \qquad (7)$$

As factor pooled from all measurements we obtained x = 2.6 [$\mathrm{kg \cdot kg^{-1} \cdot m^{-3} \cdot m^{3}}$] if soil water content is measured in $kg(H_2O)_{act} \cdot kg(H_2O)_{FC}{}^{-1}$. Note that the conversion factor is only valid for our type of soil and cannot be transferred to other experiments or field conditions.

3) I have found it hard to follow the description of the experiment 3 with holm oak, as in the Material and methods as in the Results. I advise authors to be clearer in this aspect, as the question of how to model temperature and SM is also important in the paper. From the Material and methods I don't understand if temperature sensitivity of MT emission is assessed along the whole gradient of soil water availability.

Our response: As shown in Fig. 6, the temperature sensitivity was assessed along the whole gradient except for the 2 days when systematic temperature changes were deliberately interrupted. In order to make this clearer, we modified the sentence accordingly and we added another sentence to avoid misunderstanding (see also below when the remark is repeated).

Then in the Results section, I don't find it clear whether there is an interaction between temperature and SM; it seems so in Lines 20-28 (P 13000), but not from figure 6. Finally, I don't understand why using a correction factor for MT emission in experiments 3 and 4.

Our response: There is a simultaneous action of temperature and soil moisture but there is no substantial interdependency of the impacting factors. The former is a physical principle and a reason for choosing factors in a multiplicative approach. The latter is a precondition for a multiplicative approach. The latter is written as one of the main results in the Abstract (P.

12987, line 17 – 20), noted in the Result section (P. 13001, lines 21-23) and discussed in section 4.4 "Justification of a multiplicative approach for modelling" (p. 13010).

As explanation: If a measured quantity is affected by two factors and both of them are changed simultaneously, both factors impact the measured quantity simultaneously. The impacts of both factors overlap and the impact of one of them may not be obvious. This basic logical principle is of course valid when MT emissions are the measured quantity and both, soil moisture and temperature impact this quantity (as in experiment 3) or soil moisture and light intensity impact the emissions (as in experiment 4).
Such overlap or simultaneous action is no interdependency. Interdependency of impacts means that e.g. the soil moisture would impact the temperature dependence (β) or vice versa, the actual temperature would impact soil moisture dependence, i.e. $\Delta\Theta_1$. This was not observed in our study.
May be that the referee's impression of an unclear description arose because we did not clearly enough separate between experimental observations and processed data. To avoid possible misunderstanding, the respective sentence (P. 13000, lines 24 – 25) was changed to:

<u>In the raw data</u> typical log–linear relationships between emissions and temperature were not easily observable. We therefore had to correct the data to <u>remove</u> the drought induced decrease of MT emissions over the day.

First, why leaving temperature constant below 0.02 SM? Cannot you use previous relationships of SM and MT emission at constant temperature from the previous experiments1 or 2? Or more simply, why not just simply measure MT temperature sensitivity along the whole gradient of SM? Please, can you try to clarify these questions?
Our response: the criticism is accepted. In the text we wrote that temperature was kept constant for 2 days when Θ had fallen to below 0.02 $m^3 \cdot m^{-3}$ (P.12995, lines 24-26) but at least in the text we did not explicitly give the information that the temperature was systematically changed again after these two days.
To avoid confusion the phrase "temperature was not changed for two days" was exchanged by the phrase "systematic temperature variations were interrupted for two days". A sentence was added to highlight that systematic temperature variations were started again after these two days. The sentence reads:

After these two days the chamber temperatures were again varied in the same manner as before these days.

We hope that this misunderstanding is cleared after having changed the phrase and added the sentence.

We certainly can use the relationship from other experiments but we decided using data from the same individual to diminish possible bias due to plant to plant variability.

I would expect net CO2 assimilation does not change or even decline with increasing temperature and thus de novo MT emission would be less sensitive to temperature as seedlings are more drought-stressed.
Our response: This point is well taken; however, our experimental results contradict the expectations of referee #1. Within the error limits, de-novo MT emissions from the investigated individual showed the same temperature dependence for the well watered plant

as for the drought stressed seedling. Our findings with this respect are shown in Fig. 6, mentioned in the text (P. 13001, lines 17-23), and discussed in Sect. 4.4.

Other aspects that I highlight from the review follow.

P 12992 Line 2. Why did you decide to set CO2 concentration at 350 ppm? Can you indicate the deviation from 350 along the experiment?
Our response: CO_2 *concentrations were set to 350 ppm in the plant chamber because this is similar to environmental conditions.* CO_2 *concentrations in the chamber increased when net photosynthesis was suppressed due to drought. We indicated the deviations from 350 ppm in the text. The text reads:*

CO_2 was added to the inlet air to keep the CO_2 concentrations similar to those in the environment. CO_2 concentrations at plant chamber inlet were about 385 ppm. Uptake by the plants reduced the CO_2 concentrations in the chamber to about 350 ppm when the plants were well watered. Progressing drought caused lowered net photosynthesis and CO_2 concentrations in the chamber increased near to those at chamber inlet.

P 12993 Line 5 How much the 20-30 g error is in proportion to total weight?
Our response: We now mention that this noise of 20-30 g adds an uncertainty of about $\pm 0.0012\ m^3 \cdot m^{-3}$ *to* Θ *and we have changed from giving relative errors to absolute errors.*

Compared to total amount of water in our pots (5 – 6 L), the noise of 20 – 30 g (equivalent to 20 – 30 mL, peak to peak noise) is of minor importance. The uncertainty put on the water volume measurements by this noise is ±15 mL. As a consequence, the precision of Θ *is limited to* $\pm 0.0012\ m^3 \cdot m^{-3}$ *in our pots containing ~13 L soil. As long as* Θ_1 *and* $\Delta\Theta_1$ *are much higher than* $0.0012\ m^3 \cdot m^{-3}$ *(*$\Delta\Theta_1$ *is about 50 times higher) the uncertainty put on* Θ_1 *and* $\Delta\Theta_1$ *is negligible. Compare also our new text regarding the error estimation.*

P 12994. Line5. It is dangerous to select "representative" leaves. We can subjectively over/under estimate leaf area by non-randomly sampling bigger or smaller than average leaves.
Our response: We were well aware that selecting representative leaves can cause biases and we therefore took extra care in selecting the leaves.
Nevertheless, none of results and the statements given in our manuscript with respect to the soil moisture dependence of MT emissions needs quantitative data of leaf areas. Quantities that need such leaf areas are net-photosynthesis, transpiration, and absolute emission rates. But, comparing these quantities among each other cancels out leaf area because the data are obtained simultaneously for one individual with a given leaf area. As an example: testing possible relations between e.g. net-photosynthesis and MT emissions does not require exact data on leaf area. Net-photosynthesis is related to leaf area and emission rates are related to the same leaf area. The ratio of such quantities or the delayed response of MT emissions to drought is independent of the exact leaf area.

Somewhere in the Material and methods, it should be said how many plants per species were used in the study.
Our response: thanks for the hint. A sentence is added to the material and methods section. The sentence reads:

In total 7 plants were used for the measurements: one individual each for beech, spruce, and pine and four individuals of Holm oak.

P 12997 Line 4. Why the standard emission rate of MT is considered as the average around the maximum values and not at maximum SM?
Our response: By our choice in the manuscript the normalized data are set to 1 when, according to the model they should be 1.
We will leave this as it is. Everyone who needs data on absolute emission rates for modelling purposes at high soil moisture can easily obtain such data by using the data shown in Table 2 and applying published T and PAR dependencies to adjust to the standard conditions of the respective model. Note that the temperatures listed in Table 1 are not the leaf temperatures. Leaf temperatures at $\Theta = \Theta_1$ *are 4-5 °C higher than the chamber temperatures listed in Table 1.*

P 13997 Lines 19-24. I find it surprising that severe droughts do not cause a generalized metabolic “disorder” preceding mortality that is reflected in the VOC spectrum.
Our response: We take it as positive that our experimental findings are able to surprise referee #1. It indicates new findings. However, we indeed did not observe a generalized metabolic disorder that was reflected by changes in the BVOC spectra. Maybe our drought application was not harsh enough but our intent was not to reach critical levels of drought for the plants but rather stress the plant until de-novo MT emissions were low enough to be negligible. After this level, we re-watered the plants to continue with experiments and to observe the recovery.

P 12998 Lines 6-21. Due to differences in the composition of MT emission, would not it be more practical to demonstrate drought effects on the sum of all MT instead of the dominant compound (which may change among studies)?
Our response: A valuable characteristic of a factorial approach is that absolute emissions are considered in standard emission rates (so called emission factors); the dependencies of the emissions on environmental variables such as temperature, light, or soil moisture are considered by other factors. The description of the soil moisture dependence by the function given here is independent of using an individual MT or the sum of all MT for demonstrating the dependencies.
If the use of the sum of all MT is desired, the emission rates for the sum of all MT emission are given in the 4th column of Table 2. Our description of the soil moisture dependence is not affected by this choice as long as all emissions are due to the same general mechanism. The evidence therefore that also this factorial approach is valid is given by Fig. 2. The MT emission pattern does not change at all.
Please note that this method cannot be applied to the sum of MT emissions from Scots pine and Norway spruce as emissions from both conifers contain pool emissions. We therefore gave our data on total MT emissions from conifers in the footnote to Table 2 (see our response to a remark of Rüdiger Grote with respect to pool emissions).

P 13002 Lines 19-27. It would be nice to see the data of MT emission versus SM, as for holm oak and beech in figures 5b and 4, respectively.
Our response: accepted, but we put this figure to a supplement in order not to overload the manuscript with similar looking plots. The hint to both figures is given in the respective text passage and reads:
compare Figs. S3 and S4 in the supplement

P 13003 Line 16. Plant water potential between -2 and -8 MPa is not mild drought stress; it is a severe stress even for Mediterranean species.

Our response: the assessment of drought being mild or severe depends on the quantity looked at. Compared to MT emissions, transpiration and net photosynthesis decrease earlier with progressing drought. Therefore drought may be assessed as severe when looking at transpiration and may be assessed as mild when looking at MT emissions. As Ormeño et al. (2007) describe an increase of MT (also for Q. coccifera which is a de-novo emitter), the suppressing effect on MT synthesis must have been minor. We therefore prefer to keep our categorization of the citation Ormeño et al. (2007).

P 13009 Line 15. Please say how you estimated the fraction of photosynthetic electron transport destined to MT synthesis.

Our response: As written on P. 13009, line 13, the fraction of photosynthetic electron transport ε *was determined as described in Niinemets et al. (2002):*

ε *was calculated using the equation (Eqn) 4 given therein (*$\varepsilon = (J_C + J_E) / J_T$*). The rate of photosynthetic electron transport* J_C *required to produce sugars for MT synthesis was calculated according to Eqn 2 in Niinemets et al. whereby MT emission rates were taken from our measurement,* C_i *was calculated from the* CO_2 *concentrations measured in the chamber, the measured rates of net photosynthesis and stomatal conductivity determined from the measured transpiration rates and leaf temperatures considering the different diffusion coefficients of* CO_2 *and* H_2O*, and* Γ^* *was set to 90 ppm according to a test measurement. The extra photosynthetic electron transport rate for sugar reduction (*J_E*, see Eqn 3 in Niinemets et al.) was calculated using the measured MT emission rates and setting the NADPH cost of monoterpenes to* $\delta = 28$*. The total photosynthetic electron transport rate (*J_T *in the denominator of Eqn 4, see Niinemets et al.) was approximated from (*$J_{CO2+O2} + J_E$*) (see Niinemets et al., 2002, p. 261), using the measured data for net photosynthesis, setting the rate of mitochondrial respiration continuing in the light the same as measured respiration in darkness (0.19 µmol* m^{-2} s^{-1}*) and using the same values for* C_i *and* Γ^* *as used for the calculation of* J_C*.*

According to the comments of Rüdiger Grote the respective Section 4.3 was shortened and improved semi-mechanistic models are discussed now instead of the precursor model. This does not leave space for further description of this modus operandi. As the modus operandi is well documented in the literature already, we do not give more detailed explanation on this in the manuscript.

The increasing fraction of photosynthetic electron transport destined to MT synthesis between 0.15 -0.10 soil moisture (Fig 8) does not appear to support a negative effect of drought in MT emission at this range of soil moisture (Figs 4 and 5b).

Our response: Indeed, the increasing fraction of photosynthetic electron transport indicates that there is no negative effect of drought on MT emissions for Θ *between 0.15 and 0.1* $m^3 \cdot m^{-3}$*. As obvious from Fig. 4, MT emissions still increase and net photosynthesis drops steadily (compare to our response to the next remark of referee #1).*

I miss a figure or a mention of the correlation between net CO2 assimilation and MT emission, for every species.

Our response: We are not sure if we correctly understand the point raised here:

1. *The example of European beech in Fig. 4 shows decoupling of net-photosynthesis and MT emissions.*
2. *We explicitly note the differences between both quantities in the Result section (P. 12999, lines 17 – 20).*

III. *In the discussion we highlight that the missing correlation between net-photosynthesis (or transpiration) and MT emissions prevented us from using either of them as a reference quantity.*
IV. *We write that this was observed in all experiments.*
V. *We state that decoupling of net photosynthesis and emissions under drought is already described in literature.*
(for III - V see P. 13008 lines 11-16).

As referee #1 mentioned this effect by comparing Fig. 4 to the former Fig. 8 (in the previous topic), we are not sure what the comment targets at. We refrain from showing correlation plots for quantities that are obviously decoupled.

Similarly as for Fig 6, showing "beta" dependency on SM (useful for modelling through equation 1), I would show "alfa" dependency on SM (to model through equation 2).
Our response: Yes, in principle a good idea and we also intended to show the "alpha" dependency. But this was not really helpful for the following reason. Basic difference between equations 1 and 2 is the number of parameters that have to be used for fits. While equation 1 contains only one parameter, beta, equation 2 contains parameters, alpha and c_L*. While beta is easily to obtain from fits, fits for alpha lead to large error limits in absence of light saturation (compare Fig. 7). The results obtained for alpha depend on the numerical value of* c_L*. Without fixing* c_L*, fits of alpha must lead to identical values within the error limits suggesting a negligible interdependency. But this suggestion would not be tenable just due to the large error limits. Fixing* c_L *in such fits is not a real option because the results then may become biased. Hence, this mathematical problem is unavoidable and we decided showing normalised raw data that give an unbiased impression. We will leave this figure as it is.*

Other minor appreciations are:

P 12987 Line 13. "as" is missing.
Thanks, "as" is added.

P 12990 Line 27. You previously say MT emission in conifers depends on diffusion from pools. However, you measure two conifers, and say here that you are going to study de novo MT emissions. This is later explained, but at first sight is intriguing.
Thanks, we mention this in Section Introduction now. The text reads:

By using additive terms the factorial approach for *de-novo* emissions was retained. This was confirmed by Shao et al. (2001) who used this algorithm to describe the emissions from Scots pine. Scots pine exhibits pure pool emissions, mixed pool plus *de-novo* emissions as well as a pure *de-novo* emission (Kleist et al., 2012).

P 12991 Line 18. "respectively" is missing.
Thanks, is corrected

P 12994 Lines 25-28. It seems that pine, beech and spruce seedlings were grown outside and holm oak in a growth room during acclimation. If this is correct, why setting different cultivation conditions among species?

Our response: In the western parts of Germany where the experiments were performed, pine, beech and spruce are domestic allowing to store seedlings outside. Holm oak is not domestic in Germany. To avoid possible impacts by non-natural climate such as too cold nights, Holm oaks were stored in a growth room.

P 12996 Line 16. Please indicate how you separated the weights of the pot and the plant from total weight to estimate soil weight.

Here seems to be a misunderstanding: Weights of plant and pot have to be considered when RWC is used as reference quantity but we use the volumetric water content of the soil. As explained in the Methods section (P. 12996, see also Eq. (5)), the volume of the soil is required for our reference quantity. The volume of the soil was calculated from the volume of the pot, consideration of the pot's mass was unnecessary.

For our conversion factor allowing using also RWC as reference the weight of the pot was measured and subtracted from the measured mass. The weight of the plant was neglected. This is noted in the description of Eq. (6).

Figure 1 legend. Separate "hand" and "y".

Thanks, was corrected

Figures 3 and 4. Are not values of net CO2 assimilation of beech low? Even for plants in the shade?

Our response: Within plant to plant variability these numbers fit with other data. The numbers determined for net-photosynthesis were obtained using carefully calibrated device.

Referee #2 R. Grote

We thank Rüdiger Grote for his efforts, for his positive critics, for his helpful comments in particular with respect to the literature on improved semi mechanistic models. Whenever possible we changed the text according to his remarks.

This is the presentation of a very interesting experiment and I am very thankful to the authors that they approached the laborious task to determine the relationship between drought stress and monoterpene emissions. Overall, I am confident that this work will be eagerly taken up by model developers to improve their approaches. Nevertheless, I would like to suggest some potential improvements, i.e. the presentation of more results, the consideration of relative water content as a proxy for stress, and the incorporation of some more (partly very recent) literature to enrich the discussion. One of the aspects I would like to suggest considering is the modification of the Niinemets approach presented in Morfopolous et al. (Morfopoulos et al., 2013, Morfopoulos et al., 2014). This concept has been theoretically explored by Grote et al. (Grote et al., 2014) - among other things with regard to drought stress! They find that 1) the concept allows for an increase of emissions with mild drought stress and 2) an exponential decrease of emission can be represented considering observed drought effects on photosynthesis. The presented data very nicely support this theoretical model analysis.

Our response: We added some results in particular with respect to evaluation of semi mechanistic models (Morfopolous et al., 2013, 2014; Grote et al., 2014) with our experimental data. As Grote et al. (2014) explicitly handle impacts of drought, we use the data given in Grote et al. (2014) for comparison. Indeed, this improved model predicts the measured data better than antecedent mechanistic models; however, there are still substantial differences between predictions and our results.

Our comparison is described in the Section 4.3, and, as also suggested by Rüdiger Grote, the chapter 4.3 is shortened and the former Fig. 8 is removed. The revised text now reads:

We tested whether or not semi mechanistic models can be used to describe the impacts of soil moisture on MT emissions. In a first step we looked at the increase of MT emissions during recovery. Niinemets et al. (2002) couple *de-novo* MT emissions to photosynthetic electron transport. They use the fraction of the photosynthetic electron transport necessary for MT synthesis (ε) as a surrogate for standard emissions. By keeping ε constant they closely couple isoprenoid emissions to photosynthesis. We tested this approach using the data from beech during a period of mild drought and re-watering when stomatal conductance was still reliably measurable (Fig. 3, days 0 to 11). From our data obtained during mild stress and recovery ε was calculated as described in Niinemets et al. (2002). ε was found to be constant during recovery but increased for $\Theta < 0.2$ $m^3 \cdot m^{-3}$, i.e. when photosynthesis already dropped but emissions were still not affected by the drought.

Constant ε during recovery indicates a close coupling between photosynthesis and MT emissions during this period. Contrary, the decoupling of MT emissions from photosynthesis observed with Θ falling from 0.2 to 0.1 $m^3 \cdot m^{-3}$ disturbed the relationship between ε and MT emissions.

Such decoupling was also observed for isoprene emissions and photosynthetic carbon supply and has been explained by use of alternative carbon sources for isoprene biosynthesis (Possell and Loreto, 2013 and references cited therein). This may also be the reason for decoupling of MT emissions and photosynthesis. Hence, improved semi mechanistic models (e.g. Morfopoulos et al., 2013, 2014; Grote et al., 2014) allow varying the fraction of electron transport used for MT synthesis. Such variation is requested by our results and indeed, the dependence of MT emissions on soil moisture as shown by Grote et al. (2014) matches our findings better than a description with fixed electron transport. Nevertheless, there are still differences between our data and the model predictions. Our data show a substantial shift with sustained MT emissions at already strongly suppressed net photosynthesis (see Fig. 4). Even improved semi mechanistic models overestimate the impacts of drought on *de-novo* MT emissions. In particular the later reactions of MT emissions compared to the reactions in net photosynthesis (e.g. Fig. 4) should be taken into account. In units of Θ this shift is in the range of 0.09 $m^3 \cdot m^{-3}$ and in units of RWC about 0.23 $kg \cdot kg^{-1}$.

Regarding our choice of using Θ as reference for soil moisture we refer to our response to the same remark of referee #1. To allow using our data also for other models that use RWC as reference we give a conversion factor now.

Some more specific comments

Abstract:

- I would be more careful with the word ‘explainable’. From the exceptions in the measurements it could be deduced that other reasons might also be important (see below)

Our response: Rüdiger Grote is correct; in one experiment increases of MT emissions were too high to be explained with temperature increases alone. We therefore changed this sentence by adding: “In most cases”.

The explanation why we still exclude that increases of MT emissions during moderate drought were due to a direct impact of the actual soil moisture is given below.

- Some words about the photosynthesis measurements would be appreciated. Especially because I think that the delayed increase of emission after rewetting could be linked to the response of photosynthesis which also is somewhat delayed. So in fact, this finding hint to a close relation between photosynthesis and emission that should be better considered in models.

Our response: The delayed increases of MT emissions indeed might have been caused by a delayed increase in photosynthesis. That was the reason to apply the model of Niinemets et al. (2002) and we found that the predictions of the model matched the experimental findings. Moreover, the delayed increase of MT emissions could be described using a constant fraction of photosynthetic electron transport ε and hence, even antecedent models matched

our findings. Nevertheless, during progressing drought MT emissions were decoupled from net photosynthesis (compare to our response to a similar remark of referee #1).
In the revised Section 4.3 we now cite that this is already known for isoprene emissions and has been explained by use of alternative carbon sources for isoprene biosynthesis. Accordingly alternative carbon sources may also be responsible for retained MT emissions at substantially supressed net photosynthesis. To allow for better comparison with predictions of semi mechanistic models we give an average number for the difference in the responses of the plants in net photosynthesis and MT emissions (see above).

Introduction
- P12990L2: Yes, one of them is soil moisture. However, it would be nice to mention a few others such as seasonality (leaf phenology), CO2 and/or ozone.
Our response: we added leaf phenology and CO_2 *concentrations.*

- In the overview about drought stress findings in the literature, the authors might like to consider the review done by Possell and Loreto (Possell & Loreto, 2013).
Our response: The reference is included now (Section 4.3). Thanks for helping us to better complete the reference list.

Methods
- The authors seem to have determined pool emissions as well as de-novo emissions of monoterpenes. However, the paper doesn't present a quantitative differentiation of the two. Is it possible to give a species-specific ratio of the two fractions? I would like to ask the same thing for standard emission factors.
Our response: we added data on the fraction of pool emissions in the pattern of Norway spruce and Scots pine (see also below).

- Progressing drought stress increased leaf temperature by 'additional' 2-3 °C (P12996L10). Unfortunately this not presented in a graph. Nevertheless, I would be interested in the dynamic of this increase in relation to stomata conductance (or a proxy to this such as relative transpiration rate or photosynthesis).
Our response: we added a trace showing the dynamics of net photosynthesis to Fig.1.

- It says in the paper that soil samples are taken from the pots to determine Mdry (P12996L18). Is this done for each pot individually or have the soil samples been pooled? Do you think that the sample was of the same density than the average soil density in the pots?
This is important to judge the obvious problems with the determination of soil water content.
Our response: soil samples were taken individually for each pot. In some cases different samples were taken from the same pot and indeed the data suggested different densities. This caused the main uncertainties in our estimations of Θ *and this is described in more detail now. See our response to the similar remark of referee #1 and the changes made in the text with this respect. Please note that we had no problems at all with the determination of soil water, the uncertainties given for* Θ *are not high.*

- Overall, I would recommend using relative water content as drought stress proxy – alone or in addition to absolute soil water. It is much more common in modelling approaches and more easily to transfer. In principle, soil water potential would also be an option but the necessary data to derive this on the regional or global scale are not

available. There should also be a solution to find a correction method for the 'negative values' of water content.
Our response: To allow using our data also for other models we give a number to convert from Θ *to RWC.*
With respect to the negative values of water content we refer to our more detailed description of error sources and uncertainties: The uncertainties in M_{dry} *mainly shift the* Θ *axis, they have only minor impacts on* $\Delta\Theta_1$ *and there is no need to correct a slightly negative* Θ_0*.*
Please note that the negative values we give for Θ_0 *are very low compared to* Θ *which itself is positive also in this experiment except the few data around* Θ_0*.*

Results

- Define 'green leaf volatiles' before using the expression (P12997L21)
Our response: the idiom "green leaf volatiles" was removed. We believe that it is more important to note that typical stress induced emissions were not observed and we changed the text accordingly. The text passage now reads:

Neither stress induced emissions of phenolic volatiles originating downstream of the shikimate pathway nor stress induced emissions originating from the octadecanoid pathway were observed.

- P12997L25ff: This is unclear. What are 'constant patterns' or 'emission correlations that are correlated with : : :'. Consider Rephrasing.
Our response: as emission pattern we consider the composition of the MT mix, i.e. the contribution of each MT to the emitted mix. We rephrased the passage to make this clearer now. The text now reads:

The MT emission patterns were constant for each individual Holm oak and European beech. Relating the emission rates of a given MT to those of other MT (cross correlations) emitted from the same plant yielded significant correlations with coefficients of determination always above $R^2 > 0.95$ (Fig. 2). On the one hand the high correlation showed that all MT had the same basic emission mechanism: all of them were *de-novo* emissions. On the other hand the excellent correlation was obtained including the data during severe drought. This implies that for a given plant the impacts of drought were exactly the same for emissions of each individual MT species. Therefore the effects of drought on *de-novo* MT emissions can be shown at the example of a single MT.

We also added some words in the discussion (end of Sect 4.1.2) to further explain that this finding also indicates an impact of drought on a common precursor of all MT. The added text reads:

As shown in Fig. 2, cross correlations including data obtained under severe drought led to excellent coefficients of determination implying that severe drought acts in the same manner on all MT. This can only be explained by two possibilities. Either drought suppresses all MT synthase activities in an identical manner, or affects a common precursor of all MT. While the former explanation is unlikely the latter is consistent to the findings of Grote et al. (2010) who show that MT synthase activities are unaffected by drought. The most probable explanation for the identical response of all MT emissions to the drought therefore is an impact on a common precursor.

- Why has it to be noted that acyclic ocimenes were not found (P12998L17ff)? I guess it has something to do with stress responses but the explanation is unclear.
Our response: correct, we ascribe ocimene emissions to stress. Ocimene emissions often behave very different from the cyclic monoterpenes (see also Staudt and Bertin, 1998). We explain this now in the text and highlight that our findings cannot be transferred to the ocimene emissions without further proof. The text now reads:

On the one hand correlations as shown in Fig. 2 may be disturbed in the presence of strong ocimene emissions. On the other hand we cannot report on drought impacts on ocimene emissions which may be different from that shown here for the cyclic MT.

- I would appreciate if figures like Fig. 3 would be presented also for pine and holm oak.
Our response: We added such figures for Holm oak (Fig. S1) and for Scots pine (Fig. S2) to the new supplement.

- It is not clear to me, where the variations of emissions at high water content (Fig. 4) are coming from.
Our response: The data shown in Fig. 4 for $\Theta > 0.2$ $m^3 \cdot m^{-3}$ *show no day to day variations of MT emissions. These are data taken for two different histories of soil moisture. The plant was held at high soil moisture for several days before the measurements were started (period day 0 to day 5 in Fig. 3). In the other case there was a moderate drought before the soil was re-watered (day 6 in Fig. 3).*
In the first period there was no memory regarding any possible drought before the measurements were started, MT emissions increased by about 20 % when Θ *fell from ~0.35 to ~0.12* $m^3 \cdot m^{-3}$ *(the upper cluster of points). With* Θ *falling below 0.1* $m^3 \cdot m^{-3}$ *MT decreased by about 30% due to the drought. Thereafter the plant was re-watered but MT emissions did not increase instantaneous because of the time needed for recovery. The lower cluster therefore shows data for the same plant that had experienced a moderate drought before. The increase in emissions between* $\Theta = 0.35$ *and 0.12* $m^3 \cdot m^{-3}$ *observable for the lower cluster is therefore caused by two overlapping effects: increasing leaf temperature and recovery from a preceding drought.*

In the new Fig. 4 we now use different symbols for the first and the second measurement period, respectively. We also give a more detailed description in the figure legend and we hope to have clarified this now.
We come back to this point when the increases in MT emissions according to leaf temperature increases are discussed below.

- Is it possible to present the emission factors for the sum of monoterpenes – possibly differentiated by pool- and de-novo- emissions? In the text only some relative

amounts for the compounds used in the analysis are given. This could be better presented in a table which would be beneficial for the text which is quite complicated.

Our response: All numbers given in the text and in Table 2 are for pure de-novo MT emissions. European beech and Holm oak do not exhibit pool emissions, only Scots pine and Norway spruce exhibit pool emissions. We apologize for not having mentioned this explicitly; this is corrected now. We also added the information for the conifers (for both see additional text on explanations of cross correlations).
As there are just two numbers to be added for the total MT emissions we decided to add the respective information in Table 2. To avoid possible misinterpretation we used a footnote instead of adding to Table 2 directly. In the footnote we also state that pool emissions behave differently from de-novo emissions and that the soil moisture dependence of the sum of MT emissions from the conifers cannot be treated the same way as for the 1,8- cineole emissions.

Discussion

- It would be very interesting, if temperature dependence of emission increase (P13004) could be quantified. In any case, it should be discussed that other reasons for the increase are at least possible. I am particularly thinking on the excess electron flux that is coming from the light reaction of photosynthesis and is not channelled into assimilation any more when CO2 supply is limiting. This electron supply could eventually trigger emission production (see Grote et al. 2014).

Our response: It is not easy to determine temperature dependencies from the temperature increases during progressing drought. Such increases were only 2 – 3 °C and the small dynamic range of temperature changes would cause high uncertainties of the resulting data.
We therefore used another method to exclude that direct impacts of drought are responsible for the increase of MT emissions. We applied a temperature coefficient of 0.12 K^{-1} *to calculate the hypothetical increase that is to be expected according to the increased leaf temperature. A temperature coefficient of 0.12* K^{-1} *was used because it was measured in one of our experiments (see Fig. 6). The range of expectable increases of MT emissions was 27% – 43% (=* $\exp(\beta*\Delta T)$*) which was very similar to the measured increase. It is self-evident that a number for* β *determined from the measured increase of MT emissions with drought induced increases of leaf temperature must be very similar to the assumed* β *of 0.12* K^{-1}*.*

In 6 out of 7 cases the increased leaf temperatures can easily explain the measured increases of MT emissions.

Indeed, there was one case where the increase was not explainable by temperature increase alone. In this case the estimated temperature coefficient would be ~0.5 K^{-1}*, i.e. atypically high. We therefore ascribed this high increase to another effect. Although we measured this effect for one individual of Holm oak and not for beech, the data shown in Figure 4 for beech are a good example to explain why we assumed this high increase to be due to recovery:*

The first drought applied to the beech was moderate (Θ *minimum* Θ *~ 0.1* $m^3 \cdot m^{-3}$*). When* Θ *decreased from 0.35* $m^3 \cdot m^{-3}$ *to 0.12* $m^3 \cdot m^{-3}$ *the emissions increased by about 20 % due to the increased leaf temperature. But, when* Θ *decreased to ~ 0.1* $m^3 \cdot m^{-3}$ *the MT emissions decreased by about 30% due to the drought. Re-watering did not cause a prompt increase in MT emissions and, during the following period when* Θ *again decreased from to 0.12* $m^3 \cdot m^{-3}$ *both, the recovery and the increasing leaf temperature simultaneously affected the emissions.*

Using the data from the upper cluster (triangles in the new Fig. 4) we find an increase in the range of ~ 20 %, which, at an increase of leaf temperature by about 2 °C, is easily explainable without the necessity of drought impacts. Using the data from the lower cluster (open circles) we find an increase of ~50% in the MT emissions. This would not fit to a *temperature coefficient of 0.12* K^{-1}*. However, we know that the plant suffered from drought before it was re-watered. Consecutive drought – watering – drought periods also impact the increase of MT emission measured for* Θ *falling from maximum to* Θ_1*.*

This was mentioned as reason for the high increase in MT emissions in this one case where the extraordinary high increase was observed. As this extraordinary high increase was observed once only, the other behaviour was observed in 6 cases we assessed the one case to be an outlier and not the 6 other cases.

For soil moistures above Θ_1 *direct impacts of drought on de-novo MT emissions are unimportant if existing at all. We refrain from discussing even more effects to be responsible for the observed increases besides leaf temperature and recovery.*

- P13004L17ff: Please note that this chapter discusses mild drought stress impacts. I gather that the conclusion for modeling is to describe leaf temperature more mechanistically and consider cooling by transpiration. The decreasing impact on emission should be discussed in the chapter of severe drought stress.
Our response: We agree, it would be better to have a more mechanistic description of leaf temperature. However, the respective chapter deals with the procedure used in MEGAN and how such drought induced temperature increases are considered for isoprene. We here cite the respective modus operandi and we suggest applying the same modus operandi also for de-novo MT emissions.
Only the last sentence of this chapter deals with severe stress but again this is just the modus operandi used in MEGAN and our crossover to the next section that deals with severe stress. We leave the chapter as it is.

- Regarding the impact of soil moisture (P13006L18ff), it might be good to include the data of Acosta-Navarro et al. (Acosta Navarro et al., 2014), whose estimates of the drought impact are a bit higher than those mentioned.
Our response: thanks for the hint, the estimate of Acosta Navarro is included in the respective text passage.

- Generally, the chapter 4.2 (state of the art regarding models) would benefit from citing the recent reviews of the topic by Monson et al. (Monson et al., 2012) and Grote et al. (Grote et al., 2013).
Thanks for the hint. This was the fault of the corresponding author who had overlooked this.

Our response: We changed the title of Section 4.2 from "Present state of modelling" to "Present state of modelling with MEGAN". Comparison of our results with predictions of the model of Niinemets et al. (2002) and the improvements obtained by allowing variations of the fraction of electron transport for MT synthesis (models of Morfopoulos et al., 2013, 2014 and Grote et al. 2014) are discussed in Section 4.3 now. The revised text is already given above.

- As stated at page 13007, the relative soil moisture is indeed a common index term to describe drought. The authors demonstrate that they could easily calculate this value, which I again recommend to do. The different possibilities of introducing drought stress into emission models by using this relative water content have been investigated by Grote et al. (Grote et al., 2009) and further explored by Grote et al. (Grote et al., 2010).
Our response: we added the factor allowing using RWC as reference (see above).

- At P13008L23ff the time lag between re-watering and MT emission recovery is discussed. I would like to mention that also photosynthesis is recovering and that these findings support the idea that photosynthesis and emissions are directly linked (as stated in the Niinemets model). The use of epsilon however, might indeed not be appropriate if use alone as has been demonstrated for all light-dependent isoprenoid emissions by Grote et al. (Grote et al., 2014). Given the information above, the chapter 4.3 might need a revision that could include a considerable shortening, particularly regarding the end.
Our response: chapter 4.3 is substantially revised now. We include a comparison of our data to the results shown by Grote et al. (2014) for the impact of drought, we comment on the improvement compared to the model of Niinemets et al. (2002), we note that shifts in the fraction of electron transport are more pronounced than assumed by Grote et al. (2014). The revised text is already given above.

Conclusion
- Please consider the new findings (best of our knowledge: : :) also in the conclusions.
Our response: We rephrased the respective part. The revised part now reads:

On the other hand to the best of our knowledge semi mechanistic models over predict the impacts of drought on *de-novo* MT emissions.

- P13011L23: replace ’will’ by ’might’ or similar
Our response: thanks, done

- P13011L26: as far as I recall Kleist et al. advocate a less intense increase of emission with heat rather than a suppression of MT production.

Our response: We agree, Kleist et al. advocate a less intense increase. The phrase “also suppress” was exchanged by the phrase “negatively affect”.

Figures
- Harmonize colors between Figs. 3 and 4
Our response: We do not understand this remark. Fig. 3 shows sabinene emissions in red colour and net photosynthesis in black. Fig. 4 uses the same colours, red for sabinene emissions and black for net photosynthesis.

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